

SPECIFICATION

METHOD FOR PRODUCING MODIFIED SULFUR CONTAINING BINDING AGENT AND METHOD FOR PRODUCING 5 MODIFIED SULFUR CONTAINING MATERIAL

FIELD OF ART

The present invention relates to a method for producing
a binding material containing sulfur modified with
10 dicyclopentadiene, as well as a method for producing a
material containing modified sulfur that enables
recycling of wastes and industrial by-products into
materials for civil engineering or construction.

BACKGROUND ART

15 Application of sulfur as civil engineering and
construction materials has been under research, which
makes use of its properties to melt over 119 °C and be solid
at ordinary temperatures. For example, there have been
proposed to use sulfur as a material for paving roads (US
20 Patent No. 4,290,816), a stock material for construction
materials (JP-55-49024-B), and a binding material for
sealing waste (JP-62-15274-B).

However, a binding material composed solely of sulfur
will give a molded product having sulfur exposed on its
25 outer surface, which is ignitable. Such molded product
also has various other disadvantages such as insufficient
mechanical strength and inferior resistance to sulfur-

oxidizing bacteria, so that the product has not been used widely.

In order to overcome these disadvantages, various additive compounds have been developed.

5 Dicyclopentadiene, as an example of such additive compounds, is inexpensive and economical, and is known to have good effect on mechanical strength of the molded products, as described in New Uses of Sulfur - II, 1978, p68-77. It is also known to modify the properties of
10 sulfur by adding to it vinyl toluene, dipentene, or other olefine oligomers, for use as road materials, adhesives, or sealants (JP-2-25929-B, JP-2-28529-B). Road materials containing mixed asphalt and sulfur are now in practical use.

15 Sulfur, which is known to have an application as a binding material, has been used by mixing with various aggregates to prepare molded products for civil engineering or construction materials. However, the molded products prepared with a binding material composed
20 solely of sulfur have various problems in its property, and have only limited use.

Sulfur has a flash point of 207 °C and a spontaneous ignition temperature of 245 °C, and is thus ignitable. Sulfur exposed on the surface is easy to burn and
25 disadvantageously combustible. On the other hand, sulfur exhibits high strength in a stable solid state without defect. However, sulfur solidified by cooling from a

liquid state is a mixture of rhombic, monoclinic, and amorphous sulfurs, a compositional ratio of which varies depending on the cooling conditions, as well as with the lapse of time. Thus solid sulfur in practice tends to have defects and is brittle.

Rhombic sulfur is the most stable form of solid sulfur. However, since rhombic sulfur has the highest density among the three kinds of sulfurs mentioned above, voids will form with the lapse of time, which results in reduced mechanical strength, and even cracks in an extreme case. Further, water infiltrates into the voids to dissolve the materials sealed inside, which deteriorates the hazardous substance sealability. Moreover, sulfur-oxidizing bacteria, which live in soil and water, intrude into the voids to cause corrosion on the product surfaces.

For overcoming such problems, use of dicyclopentadiene has been discussed. The reaction of dicyclopentadiene and sulfur is said to be a kind of polymerization, wherein dicyclopentadiene first reacts with sulfur, which is then polymerized by radical chain reaction. This reaction is highly exothermic, so that the temperature suddenly rises and the viscosity increases sharply. The uncontrollable reaction results in rapid solidification, and no shaping of the product is possible. Addition of olefin oligomers is a proposed solution for preventing such uncontrollable reaction (JP-2-28529-B). However, for use of dicyclopentadiene, sufficient studies have not been made

in production conditions, and the relationship between the reaction conditions, such as the dicyclopentadiene concentration and the temperature, and the desirable properties of the resulting binding material have not fully
5 been established.

When the cooled, solidified binding material is re-heated for mixing with aggregate, the polymerization reaction between sulfur and dicyclopentadiene resumes to proceed further curing. Appropriate properties of the
10 binding material for such use and the production conditions for mixing with aggregate have not yet been established.

It is not known to use a binding material modified with dicyclopentadiene for sealing wastes and industrial by-products, and the production conditions therefor have
15 not been established. Wastes and industrial by-products have generally been disposed of by landfilling or incineration, but sites for these treatment have been running short of. Thus it is demanded to recycle as much of the wastes and industrial by-products as possible. For
20 example, waste such as steel slag, coal ash, and incinerated ash, has been made into molded products, and recycled into landfilling materials for civil engineering, construction materials, and the like. In this case, mechanical strength of the molded products is required,
25 including compressive strength, bending strength, tensile strength, and impact resistance. Also required for the molded products are water sealability for preventing

elusion of heavy metal compounds contained in the industrial by-products, noncombustibility for preventing ignition by fire, and resistance to sulfur-oxidizing bacteria that cause corrosion of sulfur on the product surfaces in soil or the sea. The incinerated ash, in particular, contains hazardous substances such as heavy metals and dioxin, so that inhibition of elusion of such substances is material for the ash to be recycled into a landfilling material. Steel slag from the iron and steel industry may be used as aggregate for paving materials and civil engineering materials. However, when the slag is brought into contact with water, polysulfide is formed to generate yellowish muddy water, which has a harmful effect on the environment. Thus binding materials are demanded that make such industrial by-products fulfill the above requirements for recycling as materials for civil engineering and construction.

SUMMARY OF THE INVENTION

It is therefore an object of the present invention to provide a method for efficiently preparing a binding material containing modified sulfur with easy control of reaction. The binding material may be used for producing materials for civil engineering and construction using wastes and industrial by-products as aggregate, and is useful for giving mechanical strength, water sealability, ignition resistance, and resistance to sulfur-oxidizing bacteria to the materials, and for sealing the wastes and

industrial by-products.

It is another object of the present invention to provide a method for producing a material containing modified sulfur with easy control of reaction. The material containing modified sulfur exhibits excellent mechanical strength, water sealability, ignition resistance, and resistance to sulfur-oxidizing bacteria, even when wastes and industrial by-products are used as aggregate, and fulfills properties required for materials for civil engineering and construction.

According to the present invention, there is provided a method for preparing a binding material containing modified sulfur, comprising the steps of:

(A) mixing in a molten state 100 parts by weight of sulfur and not less than 0.1 parts by weight and less than 2 parts by weight of dicyclopentadiene at 135 to 155 °C under hermetically sealed conditions to obtain a molten material, and

(B) after a viscosity at 140 °C of said molten material falls in a range of 0.05 to 1.2 Pa·s, cooling the molten material down to a temperature not higher than 135 °C to obtain a binding material containing modified sulfur.

According to the present invention, there is also provided a method for producing a material containing modified sulfur comprising the steps of:

above step (A),

above step (B),

(C) mixing in a molten state the binding material containing modified sulfur obtained in step (B) with aggregate at a weight ratio of 1 to 5 : 5 to 9 at 135 to 155 °C, while a viscosity of the binding material at 140 °C is maintained in a range of 0.05 to 1.2 Pa·s, to obtain a molten mixture, and

(D) cooling said molten mixture obtained in step (C) down to a temperature not higher than 135 °C.

According to the present invention, there is also provided a method for producing a material containing modified sulfur comprising the steps of:

(X) mixing in a molten state sulfur, dicyclopentadiene, and aggregate at 135 to 155 °C for 0.02 to 5 hours under hermetically sealed conditions to obtain a molten mixture, and

(Y) cooling said molten mixture down to a temperature not higher than 135 °C.

PREFERRED EMBODIMENTS OF THE INVENTION

The method for preparing a binding material containing modified sulfur according to the present invention includes the steps of (A) mixing in a molten state sulfur and dicyclopentadiene at a specific ratio under specific conditions to obtain a molten material, and (B) cooling the molten material obtained in step (A) under specific conditions.

The sulfur used in the present method is ordinary elemental sulfur, and may be, for example, natural sulfur,

or sulfur obtained in desulfurization of petroleum or natural gas.

The dicyclopentadiene used in the present method may be dicyclopentadiene as a simple substance, or a mixture
5 mainly composed of monomer to tetramer of cyclopentadiene. Such mixture contains usually not less than 70 mass %, preferably not less than 85 mass% dicyclopentadiene. Thus most of the commercially-available products referred to as dicyclopentadiene may be used.

10 According to the present invention, the reaction in a molten state of dicyclopentadiene and sulfur is performed under hermetically sealed conditions in an internal mixer or the like apparatus, so that the evaporation loss of dicyclopentadiene is eliminated to improve the reaction
15 efficiency.

In step (A), the amount of dicyclopentadiene is not less than 0.1 parts by weight and less than 2 parts by weight, preferably not less than 1 part by weight and less than 2 parts by weight, based on 100 parts by weight of sulfur.

20 The amount of dicyclopentadiene affects the properties, such as noncombustibility, water sealability, and resistance to sulfur-oxidizing bacteria, of a resulting binding material as well a material containing modified sulfur produced by mixing the binding material with
25 aggregate as will be discussed later. In general, a larger amount of dicyclopentadiene will result in improved properties. However, at about 2 parts by weight of

dicyclopentadiene based on 100 parts by weight of sulfur, maximum improvement of the properties is achieved, and further increase in the amount will not result in remarkable improvement.

5 The amount of dicyclopentadiene may also be decided with reference to the controllability and duration of reaction, as well as the properties of the products to be obtained. The viscosity of molten sulfur increases with the progress of modification with dicyclopentadiene. The
10 rate of increase in viscosity relates to the amount of dicyclopentadiene, i.e., a larger amount of dicyclopentadiene will result in a higher rate of increase. For example, at 140 °C, when less than 0.1 parts by weight of dicyclopentadiene is used with respect to 100 parts by
15 weight of sulfur, the viscosity will not reach 0.1 Pa·s even in 10 hours or longer. In contrast, with not less than 2 parts by weight of dicyclopentadiene, a viscosity of 0.1 Pa·s will be achieved in 0.02 to 3 hours. With a smaller amount of dicyclopentadiene, workability during
20 the production process is better, but too small an amount is not good for efficient production in a short period of time. For giving elastic strength to a resulting product, the amount of dicyclopentadiene is preferably not less than 0.1 parts by weight and less than 2 parts by weight based
25 on 100 parts by weight of sulfur. With less than 0.1 parts by weight of dicyclopentadiene, sufficient strength cannot be given. The maximum strength is given to the

resulting elastic body with not less than 1 part by weight and less than 2 parts by weight of dicyclopentadiene based on 100 parts by weight of sulfur. With more than 2 parts by weight of dicyclopentadiene, viscosity properties are added to the elasticity to give a viscoelastic product, which is easy to distort and difficult to be damaged due to its increased viscosity. Thus the amount of dicyclopentadiene should be decided taking the above properties into consideration.

10 In step (A), the mixing in a molten state of sulfur and dicyclopentadiene under hermetically sealed conditions is performed in a temperature range of 135 to 155 °C until the viscosity of the resulting molten material at 140 °C falls in the range of 0.05 to 1.2 Pa·s. More specifically, first the sulfur is melted under heating. When solid sulfur is heated, the solid-to-liquid phase change starts at 119 °C. After the sulfur is liquefied, the entire mass is stirred, and further heated up to about 130 °C, while the viscosity of the mass is monitored with, for example, a Brookfield type viscometer. Then a predetermined amount of dicyclopentadiene is added little by little. Sulfur is not modified easily at a temperature not higher than 135 °C. That is, in the temperature range of 120 to 135 °C, sulfur and dicyclopentadiene polymerize slowly without sudden heat generation or viscosity increase, and only slight rise in temperature and viscosity is observed so that the viscosity is maintained

substantially constant. When no heat generation is confirmed, then the temperature is slowly raised to the range of 135 to 155 °C. Over 155 °C, the viscosity increases sharply and is hardly controllable. The rate of increase in viscosity depends on the reaction temperature, with higher temperature resulting in a higher rate. In view of the above, the mixing in a molten state of sulfur and dicyclopentadiene must be carried out in the temperature range of 135 to 155 °C for efficient modification of sulfur.

The duration of the mixing in a molten state depends on the amount of dicyclopentadiene and the temperature of melting. For example, when 0.2 parts by weight of dicyclopentadiene is used with respect to 100 parts by weight of sulfur, the viscosity of 0.1 Pa·s is achieved in about 15 hours at 135 °C, in about 5 hours at 140 °C, in about 2 hours at 145 °C, and in about 0.5 hours at 150 °C. In view of the temperature control and production time, a particularly preferred temperature range is 140 to 145 °C.

Completion of reaction through the mixing in a molten state may be determined by the viscosity of the molten material. The viscosity should fall in the range of 0.05 to 1.2 Pa·s at 140 °C, and the optimum viscosity is 0.08 to 0.5 Pa·s in view of the strength of molded products produced using the resulting binding material, and workability during the production process. With a

viscosity of less than 0.05 Pa·s, sufficiently high strength cannot be given to the materials for civil engineering and construction produced using the resulting binding material, and sufficient modifying effect of dicyclopentadiene cannot be obtained. The modification proceeds with the rise in viscosity, resulting in higher strength of the resulting binding material. However, above a viscosity of 1.2 Pa·s, the molten material is hard to stir and mix and its workability is remarkably lowered, while the modifying effect is saturated.

The mixing in a molten state may be performed in any conventional mixers as long as the mixer provides thorough mixing under hermetically sealed conditions. In this regard, hermetically sealed mixers for stirring liquid are particularly preferred, such as internal mixers, roll mills, drum mixers, pony mixers, ribbon mixers, homomixers, and static mixers.

In step (B), when the viscosity of the molten material falls in the above-mentioned specific range, the mixing in a molten state may be terminated, and the cooling may be carried out at a temperature below the reaction temperature, i.e., not higher than 135 °C, so as not to cause viscosity increase. The lower limit of the cooling temperature is not particularly restricted, and may be a room temperature.

The binding material prepared by the present method, which may be referred to as sulfur cement, contains

modified sulfur, wherein sulfur has been reacted with dicyclopentadiene and polymerized, and may additionally contain pure sulfur. The binding material is useful as materials for civil engineering and construction, and may
5 be mixed with various aggregate for use as paving materials, construction materials, and sealing materials for waste.

The method for producing a material containing modified sulfur according to the present invention includes: a method including step (C) of mixing in a molten
10 state the binding material obtained through above steps (A) and (B) with aggregate at a particular ratio at 135 to 155 °C, while the viscosity of the binding material at 140 °C is maintained in the range of 0.05 to 1.2 Pa·s, to obtain a molten mixture, and step (D) of cooling the molten
15 mixture obtained in step (C) down to a temperature not higher than 135 °C (referred to as a "first method" hereinbelow); and a method including step (X) of mixing in a molten state sulfur, dicyclopentadiene, and aggregate under particular conditions to obtain a molten mixture,
20 and step (Y) of cooling the molten mixture down to a temperature not higher than 135 °C (referred to as a "second method" hereinbelow).

The aggregate used in the first and second methods is not particularly limited as long as it may be used as
25 aggregate, and recyclable industrial by-products may preferably be used. Examples of such industrial by-products may include incinerated ash, incinerated fly ash,

molten fly ash generated in a high temperature melting furnace for city waste, coal ash discharged from the electric power industry and general industry, fluidized sand used in fluidized bed incinerators, soil contaminated with heavy metals, grinding waste, by-products of various metal productions, and mixtures thereof. Examples of the by-products of various metal productions may include steel slag, steel dust, ferronickel slag, aluminum dross, steel slag, and mixtures thereof. According to the present method, waste such as steel slag, incinerated ash, and coal ash, may be used as aggregate in a harmless form.

The steel slag is a by-product of the iron industry, and may include blast furnace slag, open furnace slag, converter furnace slag, and the like. The main components of the steel slag may be oxides such as silica, alumina, calcium oxide, and iron oxide, and also inorganic sulfides.

The incinerated ash is waste from various combustion furnaces such as city waste incinerators and industrial waste incinerators, and is mainly composed of oxides such as silica, alumina, calcium oxide, and iron oxide, with high contents of toxic metals, such as lead, cadmium, and arsenic. The incinerated ash has been disposed of at sanitary landfill sites where no waste water is discharged, but the present invention enables use of such incinerated ash as aggregate.

The coal ash is waste from various coal combustion furnaces for power generation, heating, and the like, and

those used for concrete or as an admixture for civil engineering materials may be used.

Examples of the aggregate used in the present invention may include aggregate other than those mentioned above, such as clay mineral, activated carbon, carbon fibers, glass fibers, vinylon fibers, aramid fibers, sand, gravel, and other equivalent inorganic and organic materials free of hazardous substances.

In step (C) of the first method, the mixing ratio of the binding material to the aggregate is 1 to 5 : 5 to 9 by weight. The maximum strength of the resulting material is achieved when the binding material is at such a ratio as to fill the voids in the aggregate consolidated to the maximum density. When the amount of the binding material is less than 10 wt%, i.e. when the amount of the aggregate is higher than 90 wt%, the surface of the inorganic material as the aggregate cannot be wet sufficiently and is left exposed, resulting in insufficient expression of the strength and incapability of maintaining the water sealability. When the amount of the binding material is higher than 50 wt%, i.e., when the amount of the aggregate is lower than 50 wt%, sufficiently high strength cannot be achieved. The mixing ratio of the binding material and the aggregate may also vary depending on the kind of aggregate, and may suitably be selected from the above-mentioned range, taking the kind of aggregate into account. For example, when the aggregate is steel slag,

the amount of aggregate may preferably be about 15 to 25 wt%.

In step (C) of mixing in a molten state the binding material and the aggregate, the viscosity of the binding material increases with time, so that it is necessary to adjust the viscosity within an optimum range for easy handling. Such an optimum viscosity range is 0.05 to 1.2 Pa·s at 140 °C. With a viscosity of less than 0.05 Pa·s, the strength of the resulting material containing modified sulfur is too low, and sufficient modifying effect is not achieved. Though higher viscosity results in higher strength of the resulting material, when the viscosity is over 1.2 Pa·s, the binding material is hard to be stirred during the production process, and its workability is remarkably impaired.

In step (C) of mixing in a molten state, both the binding material and the aggregate are preferably preheated in order to avoid temperature drop upon mixing. It is preferred to preheat the aggregate to about 120 to 155 °C, the binding material to 120 to 155 °C in as short a time as possible for avoiding progress of the reaction, and also the mixer to 120 to 155 °C. The preheated components are substantially simultaneously introduced into the mixer, and may preferably mixed at 135 to 155 °C for 5 to 30 minutes. The fluidity of the binding material and the mixing efficiency are higher at higher temperatures up to 155 °C, and the mixing in a molten state completes

in a shorter time. However, at higher temperatures, curing reaction proceeds, whereas at lower temperatures, the fluidity is lowered but the curing reaction proceeds slowly. Thus the preferred temperature range is 140 to 145 °C. In this case, the aggregate may preferably be preheated to 140 to 145 °C, and the binding material to 135 to 140 °C.

The duration of the mixing is preferably as short as possible as far as the properties of the resulting product permit, for avoiding increase in viscosity or curing of the mixture due to polymerization of sulfur and dicyclopentadiene. However, if the duration of mixing is too short, the binding material and the aggregate are not mixed thoroughly, so that the resulting material will not be given a continuous phase and will have voids or rough surfaces. With thorough mixing, the resulting material will be given a perfectly continuous phase with smooth surfaces. Thus the duration of mixing must be decided suitably depending on the properties of the material to be obtained.

In the first method, other ingredients may optionally be added to the binding material and the aggregate as desired. In this case, such other ingredients may be added after the binding material is remelted, or added before step (B) of cooling.

In the first and second methods, for mixing the system containing sulfur and dicyclopentadiene, any mixer may be

used as long as mixing under hermetically sealed conditions is provided, and for other mixing, any mixer including those do not provide hermetically sealed conditions, may be used as long a thorough mixing is provided. Solid-liquid mixers may preferably be used, such as internal mixers, roll mills, ball mills, drum mixers, screw extruders, pug mills, pony mixers, ribbon mixers, and kneaders.

In the second method, step (X) of mixing in a molten state sulfur, dicyclopentadiene, and aggregate may be carried out by a method wherein the aggregate is admixed under hermetically sealed conditions while the sulfur is being modified, or by a method including the steps of (X1) mixing in a molten state sulfur and dicyclopentadiene under hermetically sealed conditions to obtain a molten material, and (X2) admixing aggregate to the molten material to mix in a molten state under particular conditions. The sulfur, dicyclopentadiene, and aggregate used in these methods may preferably be those mentioned above, and also the amounts of these ingredients may preferably be selected from those ranges mentioned above. That is, the amount of dicyclopentadiene is usually not less than 0.1 parts by weight and less than 2 parts by weight, preferably not less than 1 part by weight and less than 2 parts by weight, based on 100 parts by weight of sulfur. The amount of the aggregate may preferably be selected suitably such that the ratio of the total amount of sulfur and

dicyclopentadiene to the amount of the aggregate is 1 to 5 : 5 to 9 by weight.

In the second method, when sulfur, dicyclopentadiene, and the aggregate are simultaneously mixed in a molten state, the objective material containing modified sulfur may be produced in one step, in contrast to the first method, wherein the binding material containing modified sulfur is first prepared. Thus the second method provides the objective material containing modified sulfur in a shorter time as a whole by a simplified production process, even the mixing in a molten state takes longer time.

In step (X) of mixing in a molten state, it is preferred to thoroughly stir or knead the molten mixture under hermetically sealed conditions so as to achieve a homogeneous temperature over the mixture. The temperature of the molten mixture is 135 to 155 °C and the duration of mixing is 0.02 to 5 hours. If the duration of mixing is less than 0.02 hours, dicyclopentadiene, sulfur, and the aggregate are not mixed thoroughly, so that the resulting material will not be given a continuous phase and will have voids or rough surfaces. With thorough mixing, the resulting material will be given a perfectly continuous phase with smooth surfaces. On the other hand, if the duration of mixing exceeds 5 hours, modification of sulfur proceeds to cause an increased viscosity, or even curing, of the modified sulfur, resulting in lowered workability.

In step (X), presence of the aggregate in the modification of sulfur with dicyclopentadiene will make it very difficult to determine the progress of the reaction between sulfur and dicyclopentadiene by directly measuring the viscosity. However, the basics of the reaction between sulfur and dicyclopentadiene are as discussed above, so that the reaction may be controlled by strictly controlling the manner and duration of the mixing in accordance with the estimated progress of sulfur modification. For example, the temperature and duration of the mixing in a molten state is 3 to 5 hours at 140 °C, and 45 to 90 minutes at 150 °C.

Step (X) of mixing in a molten state under hermetically sealed conditions may specifically be carried out, for example, by simultaneously introducing sulfur preheated to 125 to 135 °C and dicyclopentadiene melted at 40 to 50 °C into an hermetically sealed mixer preheated to 135 to 155 °C, subsequently introducing the aggregate preheated to about 125 to 155 °C, and mixing in a molten state at 135 to 155 °C for 0.02 to 5 hours. It is more preferred to preheat the hermetically sealed mixer to 140 to 150 °C, and carry out the mixing in a molten state at 145 to 155 °C. The sulfur and dicyclopentadiene are mixed in advance so as not to inhibit polymerization reaction of sulfur by the presence of aggregate.

In steps (D) and (Y) of the first and second methods, respectively, the molten mixture obtained in steps (C) and

(X), respectively, is cooled down to a temperature not higher than 135 °C. The lower limit of the cooling temperature is not particularly restricted, and may be a room temperature. In steps (D) and (Y), the cooling may
5 be carried out in a desired metal mold, a granulating machine, or a molding machine, to produce the resulting material containing modified sulfur in the form of desired molded products, pellets, granules, or particles. Before the cooling in steps (D) and (Y), when the molten mixture
10 is fluidized to a desired degree, the temperature of the molten mixture may be lowered and the mixing may be continued for a while at 120 to 135 °C, for preventing excess viscosity increase of the modified sulfur.

The granulating machine may be of any kind, for example,
15 a rolling type having a drum or a tilting pan, or a vibration type having a horizontal or tilting plate.

When the material produced by the first or second method is obtained in the form of particles, each particle has high strength, and the particle size is adjustable.
20 Thus the particulate material is suitable for use as a construction material, and may also be used in the same way as crushed stone. Further, in the material produced by the first or second method, the modified sulfur substantially seals the aggregate against contact with
25 surrounding water. The aggregate is hardly exposed outside, so that elusion of hazardous substances contained therein may be prevented to a certain extent. Thus this

material may be mixed with a cementitious material, such as cement, concrete, or gypsum, without affecting the curing behavior and the optimum moisture content of such cementitious material.

5 When a cementitious material and incinerated ash are conventionally produced into a cured product through the pozzolanic or sulfo-pozzolanic reaction, it is important to adjust the moisture content to the optimum. When incinerated ash of city waste, which is highly water-
10 absorbing, is used, it is particularly difficult to adjust the moisture content. Specifically, when incinerated ash of city waste is dried before mixing, the dried incinerated ash absorbs moisture from the cementitious mixture, leading to shortage of moisture. When incinerated ash of
15 city waste in a moist state is used, the cementitious mixture is given excess moisture. In either cases, properties of the resulting cured product as a construction material may be impaired. Further, when aggregate containing hazardous substances absorbs moisture, the
20 aggregate swells and can no longer be used as aggregate. In the material obtained by the method of the present invention, even the aggregate containing hazardous substances is made harmless using modified sulfur. Thus the present method is highly useful for recycling such
25 aggregate.

 The materials obtained by the present invention in the form of molded products may be used, for example, as panel

materials, flooring materials, wall materials, roof tiles, or underwater structures, making use of their moldability into any desired structure. When in the form of particles, the materials may be used as landfilling materials, roadbed materials, filling materials, or aggregate for concrete.

Examples

The present invention will now be explained in detail with reference to Examples and Comparative Examples, which are illustrative only and are not intended to limit the present invention in any way. The binding materials and the molded products prepared in Examples and Comparative Examples were subjected to measurements and evaluations in accordance with the following methods. The results are shown in Tables 1 to 3.

Compressive Strength: A $\phi 5 \times 10$ cm cylindrical specimen was prepared. On the seventh day from the preparation, the compressive strength of the specimen was measured using a 30-ton TENSILON compressive strength measuring equipment. The ratio of compression of the specimen until its fracture was taken as a strain ratio.

Water Absorption: A $\phi 5 \times 10$ cm cylindrical specimen was prepared, soaked in water at an ordinary temperature for a predetermined period of time, and taken out. The excess moisture on the specimen surface was wiped off, and the change in weight of the specimen was measured. The increase in weight was taken as the water content.

Resistance to Sulfur-oxidizing Bacteria: 100 ml of a

culture solution prepared by adjusting a solution composed of 2.0 g of NH_4Cl , 4.0 g of KH_2PO_4 , 0.3 g of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, 0.3 g of $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, 0.01 g of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, and 1.0 L of ion-exchanged water to pH 3.0 with hydrochloric acid, and a
5 2 cm x 2 cm x 4 cm prismatic specimen were placed in a 500 ml baffled flask, inoculated with a starter (sulfur-oxidizing bacteria, *Thiobacillus thiooxidans* IFO 12544), and subjected to bacterial culture with rolling and shaking (170 rpm) in a thermostatic chamber at 28 °C. pH change
10 and appearance of the specimen were observed after the inoculation. Here, pH drop indicates generation of sulfur ions by consumption of sulfur by the sulfur-oxidizing bacteria.

Noncombustibility: The noncombustibility was
15 evaluated in accordance with the ignitability test for evaluation of inflammable solids (Type 2 Dangerous Substance) defined in the Fire Defense Law. Specimens fallen under the category of Class 1 inflammable solids, which ignited within 3 seconds and continued to burn for
20 10 seconds or longer, and Class 2 inflammable solids, which ignited in not shorter than 3 seconds but not longer than 10 seconds and continued to burn, were indicated as
25 "inflammable", and specimens which ignited in longer than 10 seconds and specimens which did not continue to burn were indicated as "not dangerous".

Example 1

995 g of solid sulfur was placed in an internal mixer,

melted at 120 °C, and held at 130 °C. Here, the viscosity measured with a Brookfield type viscometer was 0.002 Pa·s. Then 5 g of dicyclopentadiene heated to about 50 °C to melt was added slowly, and stirred mildly for about 5 minutes. When no temperature rise was confirmed, the mixture was heated to 140 °C. The mixture started reacting, and the viscosity gradually rose. When the viscosity reached 0.1 Pa·s in about 5 hours, the heating was immediately stopped, and the resulting material was poured into a suitable mold or a container, and cooled at a room temperature to obtain binding material A.

Next, aggregate composed of 670 g of blast furnace slag and 130 g of coal ash and preheated to 140 °C, and 200 g of binding material A re-heated into a molten state were introduced substantially simultaneously into a mixer held at 140 °C. The mixture was kneaded for 20 minutes, poured into a cylindrical mold of 5 cm in diameter and 10 cm in height, and cooled to obtain a specimen. This specimen was referred to as molded product A.

20 Example 2

Binding material B and molded product B corresponding to binding material A and molded product A, respectively, were prepared in the same way as in Example 1, except that 900 g of sulfur and 10 g of dicyclopentadiene were used.

25 Example 3

Binding material C and molded product C corresponding to binding material A and molded product A, respectively,

were prepared in the same way as in Example 1, except that 981 g of sulfur and 19 g of dicyclopentadiene were used.

Comparative Example 1

5 Binding material D and molded product D both free of dicyclopentadiene, were prepared in the same way as in Example 1, except that 1000 g of sulfur and no dicyclopentadiene were used.

Example 4

10 199 g of sulfur heated to 120 °C to melt, 1 g of dicyclopentadiene heated to about 50 °C to melt, and aggregate composed of 670 g of blast furnace slag and 130 g of coal ash and preheated to 140 °C were substantially simultaneously introduced into an internal mixer held at 140 °C. The mixture was kneaded for about 5 minutes, 15 heated to 150 °C, and further kneaded at 150 °C for 60 minutes. The resulting kneaded product was poured into a cylindrical mold of 5.0 cm in diameter and 10 cm in height to cool, thereby obtaining molded product E as a specimen. The production of molded product E took 65 minutes.

20 Example 5

Molded product F corresponding to molded product E was prepared in the same way as in Example 4, except that 198 g of sulfur and 2 g of dicyclopentadiene were used. The production of molded product F took 65 minutes.

25 Example 6

Molded product G corresponding to molded product E was prepared in the same way as in Example 4, except that 197

g of sulfur and 3 g of dicyclopentadiene were used. The production of molded product G took 65 minutes.

Table 1

	Example 1	Example 2	Example 3	Comp. Ex. 1	Example 4	Example 5	Example 6
Kind of binding material	Binding Material A	Binding Material B	Binding Material C	Binding Material D	-	-	-
Compressive strength (MN/m ²)	32.9	22.7	5.8	7.4	-	-	-
Strain Ratio (%)	4.9	16.2	59.8	1.6	-	-	-
Kind of molded product	Molded product A	Molded product B	Molded product C	Molded product D	Molded product E	Molded product F	Molded product G
Compressive strength (MN/m ²)	52.5	55.5	24.0	45.0	52.2	53.8	22.3
Strain Ratio (%)	1.4	2.0	2.9	1.4	1.5	2.6	3.1
Water absorption after 33 days (%)	0.44	0.53	0.27	3.51	0.39	0.33	0.24

From Table 1, it is understood that the binding materials and molded products prepared in Examples 1 to 6 had better properties than those of Comparative Example 1 in higher compressive strength or higher strain ratio. The materials and products of Examples also preferably exhibited extremely low water absorption.

Table 2

	Example 1	Comp.Ex. 1	Example 4
Kind of binding material	Binding material A	Binding material D	-
pH at day 0	2.64	2.64	-
pH at day 45	1.23	0.81	-
Kind of molded product	Molded product A	Molded product D	Molded product E
pH at day 0	2.67	2.67	2.67
pH at day 45	2.49	1.26	2.51

From Table 2, it is understood that the binding materials and molded products prepared in Examples 1 and 4 exhibited less pH drop than those prepared in Comparative Example 1, indicating that the former had higher resistance to sulfur-oxidizing bacteria.

Table 3

Kind of molded product	Example 1		Example 2		Example 3		Example 4		Example 5		Example 6		Comp. Ex. 1	
	Molded product A		Molded product B		Molded product C		Molded product E		Molded product F		Molded product G		Molded product D	
Shape of specimen	Rear surface of hemisphere		Rear surface of hemisphere		Rear surface of hemisphere		Rear surface of hemisphere		Rear surface of hemisphere		Rear surface of hemisphere		Rear surface of hemisphere	
	Igni- tion time (sec)	Evalu- ation	Igni- tion time (sec)	Evalu- ation	Igni- tion time (sec)	Evalu- ation	Igni- tion time (sec)	Evalu- ation	Igni- tion time (sec)	Evalu- ation	Igni- tion time (sec)	Evalu- ation	Igni- tion time (sec)	Evalu- ation
Trial 1	10	x	10	x	10	x	10	x	10	x	10	x	10	○
Trial 2	10	x	10	x	10	x	10	x	10	x	10	x	8	○
Trial 3	10	x	10	x	10	x	10	x	10	x	10	x	9	○
Trial 4	10	x	10	x	10	x	10	x	10	x	10	x	10	x
Trial 5	10	x	10	x	10	x	10	x	10	x	10	x	10	x
Trial 6	10	x	10	x	10	x	10	x	10	x	10	x	8	○
Trial 7	10	x	10	x	10	x	10	x	10	x	10	x	9	○
Trial 8	10	x	10	x	10	x	10	x	10	x	10	x	8	○
Trial 9	10	x	10	x	10	x	10	x	10	x	10	x	9	○
Trial 10	10	x	10	x	10	x	10	x	10	x	10	x	8	○
Minimum ignition time	10	x	10	x	10	x	10	x	10	x	10	x	8	○
Evaluation	Not dangerous		Not dangerous		Not dangerous		Not dangerous		Not dangerous		Not dangerous		Inflammable	

x: not ignited ○: ignited

From Table 3, it is understood that the sulfur molded products prepared in Examples 1 to 6 were not inflammable and had good properties, unlike the sulfur molded product prepared in Comparative Example 1, which was observed to be inflammable.

Subsequently, each of molded products A to G prepared in the above Examples and Comparative Example was placed in a beaker to soak, and after 30 days the color change was observed. The results were that only the solution in which molded product D of Comparative Example 1 was soaked was colored in yellow, which indicated generation of yellowish muddy water, while the solutions in which molded products of Examples were soaked were not changed in color, and stayed colorless and transparent.

CLAIMS

1. A method for preparing a binding material containing modified sulfur comprising the steps of:

5 (A) mixing in a molten state 100 parts by weight of sulfur and not less than 0.1 parts by weight and less than 2 parts by weight of dicyclopentadiene at 135 to 155 °C under hermetically sealed conditions to obtain a molten material; and

10 (B) after a viscosity at 140 °C of said molten material falls in a range of 0.05 to 1.2 Pa·s, cooling said molten material down to a temperature not higher than 135 °C to obtain a binding material containing modified sulfur.

15 2. A method for producing a material containing modified sulfur comprising the steps of:

(A) mixing in a molten state 100 parts by weight of sulfur and not less than 0.1 parts by weight and less than 2 parts by weight of dicyclopentadiene at 135 to 155 °C
20 under hermetically sealed conditions to obtain a molten material;

(B) after a viscosity at 140 °C of said molten material falls in a range of 0.05 to 1.2 Pa·s, cooling said molten material down to a temperature not higher than 135 °C to
25 obtain a binding material containing modified sulfur;

(C) mixing in a molten state said binding material containing modified sulfur with aggregate at a weight ratio

of 1 to 5 : 5 to 9 at 135 to 155 °C while a viscosity of said binding material containing modified sulfur at 140 °C is maintained in a range of 0.05 to 1.2 Pa·s to obtain a molten mixture; and

5 (D) cooling said molten mixture down to a temperature not higher than 135 °C.

3. A method for producing a material containing modified sulfur comprising the steps of:

10 (X) mixing in a molten state sulfur, dicyclopentadiene, and aggregate at 135 to 155 °C for 0.02 to 5 hours under hermetically sealed conditions to obtain a molten mixture; and

(Y) cooling said molten mixture down to a temperature
15 not higher than 135 °C.

4. The method of claim 3, wherein in step (X), an amount of said dicyclopentadiene is not less than 0.1 parts by weight and less than 2 parts by weight based on 100 parts
20 by weight of sulfur, and an amount of said aggregate is such that a ratio of a total amount of sulfur and dicyclopentadiene to an amount of said aggregate is 1 to 5 : 5 to 9 by weight.

25 5. The method of claim 4, wherein said step (X) further comprises the steps of:

(X1) mixing in a molten state said sulfur and said

dicyclopentadiene under hermetically sealed conditions to obtain a molten material; and

(X2) mixing in a molten state said molten material with said aggregate at 135 to 155 °C for 0.02 to 5 hours.

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