

SPECIFICATION

METHOD FOR PRODUCING MATERIAL CONTAINING MODIFIED SULFUR

5 FIELD OF ART

 The present invention relates to 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 by using
10 a binding material containing sulfur modified with tetrahydroindene.

BACKGROUND ART

 Application of sulfur as civil engineering and construction materials has been under research, which
15 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 binding material such as a material for paving roads (US Patent No. 4,290,816), a stock material for construction materials (JP-55-49024-B),
20 and a 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 outer surface, which is ignitable. Such molded product also has various other disadvantages such as insufficient
25 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.

Dicyclopentadiene, as an example of such additive compounds, is inexpensive and economical, and is known to
5 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 sulfur by adding to it vinyl toluene, dipentene, or other
olefine oligomers, for use as road materials, adhesives,
10 or sealants (JP-2-25929-B, JP-2-28529-B). Road materials containing mixed asphalt and sulfur are now in practical use.

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

20 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 disadvantageously combustible. On the other hand, sulfur exhibits high strength in a stable solid state without
25 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.

5 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
10 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 tetrahydroindene
15 has been discussed. The reaction of tetrahydroindene and sulfur is said to be a kind of polymerization, wherein tetrahydroindene first reacts with sulfur, which is then polymerized by radical chain reaction. This reaction between tetrahydroindene and sulfur is highly exothermic,
20 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
25 for preventing such uncontrollable reaction (JP-2-28529-B). However, for use of tetrahydroindene, sufficient studies have not been made in production

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

When the cooled, solidified sulfur binding material is re-heated for mixing with aggregate, the polymerization reaction between sulfur and tetrahydroindene resumes to proceed further curing. Appropriate properties of the
10 sulfur 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 sulfur binding material modified with tetrahydroindene for sealing wastes and
15 industrial by-products, and the production conditions therefor have 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
20 as much of the wastes and industrial by-products as possible. For 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
25 this case, mechanical strength of the molded products is required, 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 producing a material containing modified sulfur with easy control. 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 producing a material containing modified sulfur, comprising the steps of:

5 (A) mixing in a molten state 100 parts by weight of sulfur and 0.1 to 25 parts by weight of tetrahydroindene at 120 to 160 °C until a viscosity of a resulting molten material at 140 °C falls in a range of 0.05 to 3.0 Pa·s,

(B) cooling said molten material down to a temperature
10 not higher than 120 °C to obtain a binding material containing modified sulfur,

(C) mixing said binding material containing modified sulfur with aggregate at a weight ratio of 1 to 5 : 9 to 5 at 120 to 160 °C to obtain a mixture, and

15 (D) cooling and solidifying said mixture.

PREFERRED EMBODIMENTS OF THE INVENTION

The present invention will now be explained in detail.

In the method for producing a material containing modified sulfur according to the present invention, first,
20 step (A) of mixing in a molten state 100 parts by weight of sulfur and 0.1 to 25 parts by weight of tetrahydroindene at 120 to 160 °C until the viscosity of the resulting molten material at 140 °C falls in a range of 0.05 to 3.0 Pa·s, and step (B) of cooling the molten material down to a
25 temperature not higher than 120 °C, are performed, to obtain a binding material containing modified sulfur.

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.

5 The tetrahydroindene used in the present method may be tetrahydroindene alone, or a mixture of tetrahydroindene and one or more members selected from the group consisting of cyclopentadiene as a simple substance, polymers of cyclopentadiene and butadiene, dicyclopentadiene, and a dimer to tetramer of these. The
10 tetrahydroindene used in the present invention includes the above mixture having a tetrahydroindene content of usually not lower than 50 mass %, preferably not lower than 65 mass %. Thus most of the commercially available products referred to as tetrahydroindene, and by-product
15 oils discharged from ethylnorbornene production plants may be used as the tetrahydroindene.

The amount of tetrahydroindene is usually 0.1 to 25 parts by weight, preferably 0.3 to 5 parts by weight, based on 100 parts by weight of sulfur. The amount of
20 tetrahydroindene affects the improvement in properties, such as noncombustibility, water sealability, and resistance to sulfur-oxidizing bacteria, of a resulting material containing modified sulfur. In general, a larger amount of tetrahydroindene will result in improved
25 properties. However, at about 10 parts by weight of tetrahydroindene 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.

The amount of tetrahydroindene may also be decided with reference to the controllability in the production and the 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 tetrahydroindene. The rate of increase in viscosity relates to the amount of tetrahydroindene, i.e., a larger amount of tetrahydroindene will result in a higher rate of increase. For example, at 140 °C, when less than 0.1 parts by weight of tetrahydroindene is used with respect to 100 parts by weight of sulfur, the viscosity will not reach 0.05 Pa·s even in 3 hours of mixing or longer. In contrast, with not less than 10 parts by weight of tetrahydroindene, a viscosity of 0.05 Pa·s will be achieved in 0.1 to 1 hour.

With a smaller amount of tetrahydroindene, workability during 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 tetrahydroindene is preferably 0.3 to 5 parts by weight based on 100 parts by weight of sulfur. With less than 0.3 parts by weight of tetrahydroindene, sufficient strength cannot be given. The maximum strength is given to the resulting binding material containing modified sulfur with 0.3 to 5 parts by weight

of tetrahydroindene based on 100 parts by weight of sulfur. With more than 10 parts by weight of tetrahydroindene, viscosity properties are added to the elasticity, so that the resulting binding material containing modified sulfur becomes a viscoelastic product, which is easy to distort and difficult to be damaged due to its increased viscosity. Further, with more than 25 parts by weight of tetrahydroindene, viscosity properties are remarkably exhibited, and the viscosity increase rate during the production is high, resulting in difficulties in reaction control.

The mixing in a molten state of sulfur and tetrahydroindene may be performed in apparatus equipped with a hermetically sealed stirring vessel, so that sulfur is sufficiently modified with a small amount of tetrahydroindene. With such apparatus, evaporation loss of tetrahydroindene due to the heat from the molten sulfur may be inhibited. Thus, using such apparatus, properties of sulfur may be improved effectively with only 0.1 to 2 parts by weight of tetrahydroindene based on 100 parts by weight of sulfur. When the apparatus equipped with a hermetically sealed stirring vessel is not used, more than 2 parts by weight of tetrahydroindene may be needed based on 100 parts by weight of sulfur for giving sufficient sulfur modifying effect.

After the commencement of the reaction between sulfur and tetrahydroindene, evaporation of tetrahydroindene is

no longer a problem, so that the mixing in a molten state is not necessarily performed in the hermetically sealed stirring vessel.

The amount of tetrahydroindene may be determined in
5 view of the above properties.

In step (A), the mixing in a molten state of sulfur and tetrahydroindene is performed in a temperature range of 120 to 160 °C until the viscosity of the resulting molten material at 140 °C falls in the range of 0.05 to 3.0 Pa·s.
10 More specifically, first 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
15 a suitable viscometer, for example, a Brookfield type viscometer. Then a predetermined amount of tetrahydroindene is added little by little. Sulfur is not modified easily at a temperature not higher than 125 °C. That is, in the temperature range of 120 to 135 °C, sulfur
20 and tetrahydroindene 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
25 slowly raised. Over 155 °C, the viscosity tends to increase sharply and is hardly controllable. This tendency is more remarkable over 160 °C. 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 tetrahydroindene may preferably be carried out in the
5 temperature range of 120 to 155 °C for efficient modification of sulfur.

The duration of the mixing in a molten state depends on the amount of tetrahydroindene and the temperature of melting. For example, when 5 parts by weight of
10 tetrahydroindene is used with respect to 100 parts by weight of sulfur, the viscosity of 0.1 Pa·s is achieved in about 7 hours at 130 °C, in about 2 hours at 140 °C, in about 1 hour at 145 °C, and in about 0.2 hours at 150 °C. In view of the temperature control and production time,
15 a particularly preferred temperature range for the mixing in a molten state is 130 to 140 °C.

The reaction may preferably be terminated at a time point where the viscosity of the molten material at 140 °C falls in the range of 0.05 to 3.0 Pa·s, and the
20 comprehensively optimum viscosity at 140 °C is 0.1 to 1.5 Pa·s in view of the strength of the material containing modified sulfur and other molded products produced with the binding material containing modified sulfur, and workability during the production process. With a
25 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

material containing modified sulfur, and sufficient
modifying effect of tetrahydroindene cannot be obtained.
The modification proceeds with the rise in viscosity,
resulting in higher strength of the resulting binding
5 material containing modified sulfur. However, above a
viscosity of 3.0 Pa·s, the molten material is hard to stir
and mix and its workability is remarkably lowered, while
the modifying effect is saturated.

The conditions and the termination of the mixing in
10 a molten state in step (A) are decided in advance by
preliminarily measurement of the viscosity during the
mixing in a molten state, depending on the apparatus to
be used or the kind and amount of each component, taking
the above factors into consideration. Thus it is not
15 always necessary to measure the viscosity during the actual
step (A).

The mixing in a molten state in step (A) may be
performed in any conventional mixers as long as the mixer
provides thorough mixing. In this regard, mixers for
20 stirring liquid are particularly preferred, such as
internal mixers, roll mills, drum mixers, pony mixers,
ribbon mixers, homomixers, and static mixers. When the
amount of tetrahydroindene used is 0.1 to 2 parts by weight
based on 100 parts by weight of sulfur, apparatus equipped
25 with a hermetically sealed stirring vessel is preferably
used as a mixer, and a static mixer is particularly
preferred in view of the stirring efficiency.

In step (B) of the present method, after the termination of the mixing in a molten state in step (A), the resulting molten material is cooled to a temperature below the reaction temperature, usually not higher than 120 °C, so as not to cause viscosity increase, to thereby obtain the objective binding material containing modified sulfur.

The binding material containing modified sulfur obtained in step (B) is modified sulfur wherein sulfur has been reacted with tetrahydroindene and polymerized, and may contain pure sulfur. This binding material may usually be referred to as sulfur cement or sulfur binder. The binding material is useful as materials for civil engineering and construction, and may be mixed with various aggregate for use as paving materials, construction materials, and sealing materials for waste.

According to the present invention, next, step (C) of mixing the binding material containing modified sulfur obtained in step (B) with aggregate at a particular ratio at 120 to 160 °C to obtain a mixture, and step (D) of cooling and solidifying the mixture, are performed to obtain the objective material containing modified sulfur.

The aggregate used in step (C) is not particularly limited as long as it may be used as 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,

5 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

10 such as steel slag, incinerated ash, and coal ash, may be used as aggregate in a harmless form.

The steel slag may be a by-product of the iron industry, such as blast furnace slag discharged from a blast furnace, open furnace slag discharged from an open furnace,

15 converter furnace slag discharged from a converter furnace, 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
20 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 toxic metals, such as lead, cadmium, and arsenic. Most of the incinerated ash is disposed of at sanitary landfill
25 sites where no waste water is discharged, but the present invention enables use of such incinerated ash as aggregate.

The coal ash includes those discharged from various

coal combustion furnaces for power generation, heating, and the like, which are conventionally used as an admixture for concrete or civil engineering materials.

5 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.

10 In step (C), the mixing ratio of the binding material containing modified sulfur to the aggregate is 1 to 5 : 9 to 5 by weight. The binding material containing modified sulfur is most preferably at such a ratio as to fill the voids in the aggregate consolidated to the maximum density
15 for improving the strength of the resulting material containing modified sulfur. When the amount of the binding material containing modified sulfur is less than 10 wt%, i.e. when the amount of the aggregate is higher than 90 wt%, the surface of the aggregate cannot be wet
20 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 containing modified sulfur is higher than 50 wt%, i.e., when the amount of the aggregate is lower
25 than 50 wt%, the strength tends to be lowered, approximating the properties of the binding material containing modified sulfur per se.

The mixing ratio of the binding material containing modified sulfur 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 75 to 85 wt%.

In step (C), the viscosity of the binding material containing modified sulfur during the mixing 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 3.0 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 by the binding material containing modified sulfur may not be achieved. Though higher viscosity results in higher strength of the resulting material containing modified sulfur, when the viscosity is over 3.0 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, both the binding material containing modified sulfur 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 containing modified sulfur 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 mixing in step (C) may be performed, for example, by substantially simultaneously introducing the preheated components into a mixer, and mixing usually at 120 to 160 °C, preferably at 130 to 140 °C, for 5 to 30 minutes.

The temperature for the mixing in step (C) is not higher than 155 °C. At higher temperatures, the fluidity of the binding material containing modified sulfur is higher, and the mixing is more effective and 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 mixing in step (C) is preferably performed at 130 to 140 °C in a mixer preheated to 130 to 140 °C. In this case, the aggregate may preferably be preheated to 130 to 140 °C, and the binding material containing modified sulfur to 125 to 140 °C.

The duration of the mixing in step (C) is preferably as short as the properties of the resulting product permit, for avoiding increase in viscosity or curing of the mixture due to polymerization of sulfur and tetrahydroindene. However, if the duration of mixing is too short, the binding material containing modified 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. Thus the duration of mixing must be decided suitably depending on the properties of the material containing modified sulfur to be obtained.

5 In step (C), other ingredients may optionally be added to the binding material containing modified sulfur and the aggregate as desired. In this case, such other ingredients may be added, for example, after the binding material containing modified sulfur is remelted, or before
10 step (D) of cooling and solidifying the mixture.

 The mixer used in step (C) is not particularly limited as long as thorough mixing is provided, and may preferably be a solid-liquid mixer, such as internal mixers, roll mills, ball mills, drum mixers, screw extruders, pug mills,
15 pony mixers, ribbon mixers, and kneaders. When the amount of tetrahydroindene is 0.1 to 2 parts by weight based on 100 parts by weight of sulfur, it is preferred to use a mixer equipped with a hermetically sealed stirring vessel.

 Step (D) of cooling and solidifying may be performed,
20 for example, by pouring the mixture obtained in step (C) into a mold of a desired shape, and cooling and solidifying the same, or by cooling and solidifying the mixture obtained in step (C) while the mixture is granulated in a granulating machine. Before the cooling and
25 solidifying, when the mixture is fluidized to a desired degree, the temperature of the mixture may be lowered and the mixing may be continued for a while at 120 to 130 °C,

for preventing excess viscosity increase of the modified sulfur in the mixture. By such cooling and solidifying, the material containing modified sulfur of a desired shape may be obtained, such as molded products, pellets, crushed materials, or particles. The crushed materials may be obtained, for example, by cooling and solidifying the mixture obtained in step (C) into amorphous bulk solid, and crushing the solid.

The granulating machine used for producing granules is not particularly limited, and a rolling type granulating machine having a drum or a tilting pan, or a vibration type granulating machine having a horizontal or tilting plate, may be used.

When the material containing modified sulfur obtained by the present method is in the form of particles obtained by granulating, each particle has high strength, and the particle size is adjustable. Thus these particulate materials are suitable for use as a construction material, and may also be used in the same way as crushed stone.

Further, in the material containing modified sulfur obtained by the present method, the sulfur substantially seals the aggregate against contact with surrounding water. The aggregate is thus hardly exposed outside, so that elusion of hazardous substances contained therein may be prevented to a certain extent.

Thus the material containing modified sulfur obtained by the present invention may be used by mixing 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-absorbing, is used, it is particularly difficult to adjust
10 the moisture content. For example, 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 city waste in a moist state is used, the cementitious
15 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 aggregate swells and can no longer be used as aggregate.

20 With the binding material containing modified sulfur and the material containing modified sulfur obtained by the present invention, even the aggregate containing hazardous substances is made harmless. Thus the present method is highly useful for recycling such aggregate.

25 The material containing modified sulfur obtained by the present invention, when in the form of a molded product, 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 material may be used as landfilling materials, roadbed materials, filling materials, or aggregate for concrete.

The material containing modified sulfur may alternatively be produced by a method including the steps of (C-1) mixing sulfur, tetrahydroindene, and aggregate at 120 to 160 °C for 0.01 to 3 hours to obtain a mixture, and (D-1) cooling and solidifying the mixture.

The mixing in step (C-1) may be performed by mixing sulfur, tetrahydroindene, and aggregate in the above temperature range to simultaneously effect the mixing of the aggregate and the modification of sulfur; or by mixing in a molten state sulfur and tetrahydroindene in advance to start the modification of sulfur first, and then adding aggregate for further mixing. The sulfur, tetrahydroindene, and aggregate used in this method are preferably similar to those used in the present method discussed above. The amount of each material used is preferably selected from the range similar to those in the method of the present invention. Specifically, the amount of tetrahydroindene is 0.1 to 25 parts by weight, preferably 0.3 to 5 parts by weight, based on 100 parts by weight of sulfur. In particular, when the apparatus equipped with a hermetically sealed stirring vessel is used, which may be used for producing the binding material

containing modified sulfur mentioned above, evaporation loss of tetrahydroindene due to the heat from the molten sulfur may be inhibited. With such apparatus, properties of sulfur may be improved with tetrahydroindene in an amount as small as 0.1 to 2 parts by weight based on 100 parts by weight of sulfur. Thus the amount of tetrahydroindene may be decided taking these properties into consideration. The amount of aggregate may suitably be selected depending on its kind so that the weight ratio of the binding material containing modified sulfur and the aggregate is 1 to 5 : 9 to 5.

In step (C-1), when sulfur, tetrahydroindene, and aggregate are simultaneously mixed, the objective material containing modified sulfur may be produced in one step, in contrast to the method of the present invention, wherein the binding material containing modified sulfur is first prepared. Thus this method enables the mixing of aggregate simultaneously with the modification of sulfur, and provides the material containing modified sulfur in a shorter time as a whole by a simplified production process, even the mixing takes longer time.

In step (C-1) of mixing, it is preferred to thoroughly stir or knead the molten mixture so as to achieve a homogeneous temperature over the mixture. The temperature of the molten mixture is 120 to 160 °C and the duration of mixing is usually 0.01 to 3 hours. If the duration of mixing is less than 0.01 hours,

tetrahydroindene, 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
5 will be given a perfectly continuous phase with smooth surfaces. On the other hand, if the duration of mixing exceeds 3 hours, modification of sulfur proceeds to cause an increased viscosity, or even curing, of the modified sulfur, resulting in lowered workability.

10 In step (C-1), presence of the aggregate in the modification of sulfur with tetrahydroindene will make it very difficult to determine the progress of the reaction between sulfur and tetrahydroindene by directly measuring the viscosity. However, the basics of the reaction
15 between sulfur and tetrahydroindene are as discussed above, so that the reaction may be controlled by strictly controlling the temperature, manner, and duration of the mixing in accordance with the estimated progress of sulfur modification. For example, the temperature and duration
20 of the mixing is 1 to 3 hours at 130 °C, and 15 to 40 minutes at 140 °C.

Step (C-1) of mixing may specifically be carried out, for example, by simultaneously introducing sulfur preheated to 125 to 135 °C and tetrahydroindene melted at
25 40 to 50 °C into a mixer preheated to 120 to 160 °C, subsequently introducing the aggregate preheated to about 125 to 155 °C, and mixing at 120 to 160 °C for 0.01 to 3

hours. It is more preferred to preheat the mixer to 130 to 140 °C, and carry out the mixing at 125 to 135 °C. The sulfur and tetrahydroindene are mixed in advance so as not to inhibit polymerization reaction of sulfur by the presence of aggregate.

The mixer used for the mixing in step (C-1) may be selected from those mentioned for step (C) above.

Step (D-1) of cooling and solidifying is identical with step (D) of the method of the present invention, except that the mixture obtained in step (C) is replaced with the mixture obtained in step (C-1), so that the conditions and apparatus may preferably be the same as those mentioned for step (D).

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, Referential 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: A $2 \text{ cm} \times 2 \text{ cm} \times 4 \text{ cm}$ prismatic specimen and 100 ml of a culture solution (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 $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, 1.0 L of ion-exchanged water, pH adjusted to 3.0 with hydrochloric acid) 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 at 170 rpm in a thermostatic chamber at 28 °C. pH change and appearance of the specimen were observed after the inoculation. Here, pH drop indicates generation of sulfate ions by consumption of sulfur by the sulfur-oxidizing bacteria.

Noncombustibility: The noncombustibility was 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

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 "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

950 g of solid sulfur was placed in a mixer, melted at 140 °C, and held at 135 °C. Here, the viscosity measured with a Brookfield type viscometer was 0.002 Pa·s. Then 50 g of tetrahydroindene 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 1.0 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 at 130 °C 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). The viscosity at 140 °C of the binding material (B) in a molten

state during the 20-minute kneading was within the range of 0.5 to 3.0 Pa·s.

Example 2

Sulfur melted in a tank held at 140 °C and
5 tetrahydroindene were supplied to a static mixer
(manufactured by NORITAKE Co., LIMITED, T3-17R-2PT) held
at 130 °C at a flow rate of 66g/min and 0.7 g/min,
respectively, using metering pumps, and stirred in the
mixer. Then the mixture was passed through a duct of the
10 static mixer held at 130 °C over 9 minutes of residence
time. The resulting molten material was poured into a
suitable mold or a container, and cooled at a room
temperature to obtain binding material (B). Here, the
viscosity at 140 °C of the molten material passing through
15 the duct was within the range of 0.1 to 1.5 Pa·s.

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 (B) reheated at 130 °C into a molten
state were introduced substantially simultaneously into
20 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 (B). The
viscosity at 140 °C of the binding material (B) in a molten
25 state during the 20-minute kneading was within the range
of 0.1 to 3.0 Pa·s.

From this example, it is understood that a molded

product of sufficient properties may be obtained with a small amount of tetrahydroindene by using a static mixer.

Example 3

Procedure of Example 1 was followed, except that 800
5 g of sulfur and 200 g of tetrahydroindene were used, to prepare corresponding binding material (C) and molded product (C).

Comparative Example 1

1000 g of solid sulfur was placed in a mixer, melted
10 at 140 °C, and held at 135 °C. Then the sulfur was heated to 140 °C, and stirred for about 5 hours at this temperature. Then the heating was stopped, and the resulting material was poured into a suitable mold or a container, and cooled at a room temperature to obtain binding material (D). Next,
15 procedure of Example 1 was followed except that binding material (D) was used, to prepare molded product (D) without tetrahydroindene.

Referential Example 1

190 g of sulfur heated to 120 °C to melt, 10 g of
20 tetrahydroindene heated to about 50 °C to melt, and 670 g of blast furnace slag and 130 g of coal ash both preheated at 140 °C were introduced substantially simultaneously into a mixer held at 140 °C. The mixture was kneaded for about 5 minutes, heated to 150 °C, and further kneaded for
25 60 minutes. The resulting mixture was poured into a cylindrical mold of 2.5 cm in diameter and 10 cm in height, and cooled to obtain a specimen, which was referred to as

molded product (E). The production of molded product (E) took 65 minutes.

Referential Example 2

Procedure of Referential Example 1 was followed,
5 except that 180 g of sulfur and 20 g of tetrahydroindene were used, to prepare corresponding molded product (F). The production of molded product (F) took 65 minutes.

Referential Example 3

Procedure of Referential Example 1 was followed,
10 except that 160 g of sulfur and 40 g of tetrahydroindene were used, to prepare corresponding molded product (G). The production of molded product (G) took 65 minutes.

Table 1

	Example 1	Example 2	Example 3	Comp.Ex. 1
Kind of binding material	Binding Material (A)	Binding Material (B)	Binding Material (C)	Binding Material (D)
Compressive strength (MN/m ²)	32.9	35.7	8.8	7.4
Strain Ratio (%)	4.9	5.2	49.8	1.6
Kind of molded product	Molded product (A)	Molded product (B)	Molded product (C)	Molded product (D)
Compressive strength (MN/m ²)	64.5	66.5	27.5	45.0
Strain Ratio (%)	1.4	1.5	2.9	1.4
Water absorption after 33 days (%)	0.44	0.43	0.27	3.51

15

Table 2

	Referential Example 1	Referential Example 2	Referential Example 3
Kind of binding material	-	-	-
Compressive strength (MN/m ²)	-	-	-
Strain Ratio (%)	-	-	-
Kind of molded product	Molded product (E)	Molded product (F)	Molded product (G)
Compressive strength (MN/m ²)	62.4	62.8	23.4
Strain Ratio (%)	1.5	1.6	3.1
Water absorption after 33 days (%)	0.40	0.36	0.24

Table 3

	Example 1	Comparative Example 1	Referential Example 1
Kind of binding material	Binding material (A)	Binding material (D)	-
Day 0	2.64	2.64	-
Day 45	1.34	0.81	-
Kind of molded product	Molded product (A)	Molded product (D)	Molded product (E)
Day 0	2.67	2.67	2.67
Day 45	2.55	1.26	2.52

Table 3

Kind of molded product	Example 1		Example 2		Example 3		Referential Example 1		Referential Example 2		Referential Example 3		Comparative Example 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	-	10	-	10	-	10	-	10	-	10	-	10	+
Trial 2	10	-	10	-	10	-	10	-	10	-	10	-	8	+
Trial 3	10	-	10	-	10	-	10	-	10	-	10	-	9	+
Trial 4	10	-	10	-	10	-	10	-	10	-	10	-	10	-
Trial 5	10	-	10	-	10	-	10	-	10	-	10	-	10	-
Trial 6	10	-	10	-	10	-	10	-	10	-	10	-	8	+
Trial 7	10	-	10	-	10	-	10	-	10	-	10	-	9	+
Trial 8	10	-	10	-	10	-	10	-	10	-	10	-	8	+
Trial 9	10	-	10	-	10	-	10	-	10	-	10	-	9	+
Trial 10	10	-	10	-	10	-	10	-	10	-	10	-	8	+
Minimum ignition time	10	-	10	-	10	-	10	-	10	-	10	-	8	+
Evaluation	Not dangerous		Not dangerous		Not dangerous		Not dangerous		Not dangerous		Not dangerous		Inflammable	

- : not ignited + : ignited

From Tables 1 and 2, it is understood that the binding materials containing modified sulfur and the materials containing modified sulfur prepared in Examples 1 to 3 and Referential Examples 1 to 3 had better properties than those of Comparative Example 1 in higher compressive strength or higher strain ratio. The water absorption was also extremely low, which is advantageous.

From Table 3, it is understood that the binding materials containing modified sulfur and the materials containing modified sulfur prepared in Example 1 and Referential Example 1 exhibited less pH drop than those prepared in Comparative Example 1, indicating that the former two had higher resistance to sulfur-oxidizing bacteria.

From Table 4, it is understood that the materials containing modified sulfur prepared in Examples 1 to 3 and Referential Examples 1 to 3 were not inflammable and had good properties, unlike the material containing sulfur prepared in Comparative Example 1, which was observed to be inflammable.

Subsequently, each of molded products (A) to (G) prepared above 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 and

Referential Examples were soaked were not changed in color,
and stayed colorless and transparent.

CLAIMS

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

5 (A) mixing in a molten state 100 parts by weight of sulfur and 0.1 to 25 parts by weight of tetrahydroindene at 120 to 160 °C until a viscosity of a resulting molten material at 140 °C falls in a range of 0.05 to 3.0 Pa·s,

10 (B) cooling said molten material down to a temperature not higher than 120 °C to obtain a binding material containing modified sulfur,

(C) mixing said binding material containing modified sulfur with aggregate at a weight ratio of 1 to 5 : 9 to 5 at 120 to 160 °C to obtain a mixture, and

15 (D) cooling and solidifying said mixture.

2. The method of claim 1, wherein said step (A) of mixing in a molten state is performed in apparatus equipped with a hermetically sealed stirring vessel.

20 3. The method of claim 2, wherein an amount of tetrahydroindene in step (A) of mixing in a molten state is 0.1 to 2.0 parts by weight.

25 4. The method of claim 1, wherein a duration of said mixing in step (C) is 5 to 30 minutes.

5. The method of claim 1, wherein said mixing in step (C)

is performed under conditions to keep a viscosity at 140 °C of the binding material containing modified sulfur in a molten state within a range of 0.05 to 3.0 Pa·s.

- 5 6. The method of claim 1, wherein said aggregate comprises industrial by-products selected from the group consisting of incinerated ash, incinerated fly ash, molten fly ash, coal ash, fluidized sand, soil contaminated with heavy metals, grinding waste, steel slag, steel dust,
10 ferronickel slag, aluminum dross, steel slag, and mixtures thereof.