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**ALKALINE RESOL PHENOL-ALDEHYDE RESIN BINDER COMPOSITIONS**

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(56) Prior Art Documents  
**US 4780489  
US 4977209  
US 4985489**

(57) Suitable oxyanions include borate, stannate and aluminate.

#### **CLAIM**

1. A binder composition comprising an alkaline aqueous solution of a resol phenol-aldehyde resin and an oxyanion which can form a stable complex with the resin, the amount of alkali present in the solution is sufficient to substantially prevent stable complex formation between the resin and the oxyanion, wherein the molar ratio of alkali to phenol is from 1.5:1 to 2.5:1 and the binder composition also contains phenyl monoethylene glycol monoether.

9. A process for the production of an article of bonded particulate material comprising forming to the desired shape a mixture of particulate material and a binder composition comprising an alkaline aqueous solution of a resol phenol-aldehyde resin having an alkali to phenol molar ratio of from 1.5:1 to 2.5:1, an oxyanion which can form a stable complex with the resin, and phenyl monoethylene glycol monoether, and passing carbon dioxide gas through the formed shape so as to cause the oxyanion to form a stable complex with the resin, and thereby to cure the resin.

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**ORIGINAL  
COMPLETE SPECIFICATION  
STANDARD PATENT**

Invention Title: **ALKALINE RESOL PHENOL-ALDEHYDE RESIN  
BINDER COMPOSITIONS**

The following statement is a full description of this invention, including the best method of performing it known to us:

GH&CO REF: 13583-DJ:PJW:RK

ALKALINE RESOL PHENOL-ALDEHYDE  
RESIN BINDER COMPOSITIONS

This invention relates to alkaline resol phenol-aldehyde binder compositions and their use in the production of articles of bonded particulate material such as foundry moulds or cores.

European Patent Application Publication No. 0323096A describes a binder composition comprising an alkaline aqueous solution of a resol phenol-aldehyde resin and an oxyanion which can form a stable complex formation between the resin and the oxyanion. EP 0323096A also describes a process for the production of an article of bonded particulate material, such as a foundry mould or core, in which a mixture of particulate material and the binder composition is formed to a desired shape, and carbon dioxide gas is then passed through the formed shape so as to cause the oxyanion to form a stable complex with the resin and thereby to cure the resin.

It has now been found that the performance of the binder composition can be improved if the binder composition also contains phenyl monoethylene glycol monoether.

According to the present invention there is provided a binder composition comprising an alkaline aqueous solution of a resol phenol-aldehyde resin and an oxyanion which can form a stable complex with the resin, the amount of alkali present in the solution being sufficient to substantially prevent stable complex formation between the resin and the oxyanion, wherein the molar ratio of alkali to phenol is from 1.5:1 to 2.5:1 and the binder composition also contains phenyl monoethylene glycol monoether.

According to a further feature of the invention there is provided a process for the production of an article of bonded particulate material comprising forming to the desired shape a mixture of particulate material and a binder composition comprising an alkaline



aqueous solution of a resol phenol-aldehyde resin having an alkali to phenol molar ratio of from 1.5:1 to 2.5:1, an oxyanion which can form a stable complex with the resin, and phenyl monoethylene glycol monoether, and passing carbon dioxide gas through the formed shape so as to cause the oxyanion to form a stable complex with the resin, and thereby to cure the resin.

The binder composition and the process of the invention are of particular value for making foundry moulds and cores and it is with reference to that application that the invention will be described.

Suitable phenol-aldehyde resins and oxyanions for use in the binder compositions of the invention, and suitable methods for producing the phenol-aldehyde resin are described in Australian Patent No. 605943 the disclosure of which is incorporated herein by reference.

Suitable oxyanions include borate, stannate and aluminate.

The phenyl monoethylene glycol monoether may be used as the pure compound or as a commercially available material which also contains phenol diethylene glycol monoether as an impurity.

The optimum amount of phenyl monoethylene glycol monoether contained in the binder composition will vary depending on the composition of the resin, but will usually be within the range of 1% - 10% by weight, preferably 2 - 5%, based on the weight of the binder composition.

The presence of the phenyl monoethylene glycol monoether may have one or more beneficial effects on the performance of the binder composition as a binder for making foundry moulds and cores, depending on the composition of the particular resin.



The beneficial effects include:-

- (i) improved mould or core strength immediately after gassing with carbon dioxide gas.
- (ii) improved strength after gassed moulds or cores have been stored before use, for example for up to 24 hours or longer.
- (iii) improved strength of moulds or cores which have been coated with an alcohol based coating which has been dried by burning off the alcohol, prior to storage of the moulds or cores.
- (iv) improved mixed sand flowability.
- (v) improved mould or core surface finish and edge hardness.

The binder composition of the invention preferably also contains a silane such as gamma-aminopropyltrimethoxysilane, N-(2-aminoethyl)-3-aminopropyltrimethoxysilane, phenol trimethoxysilane or gammaglycidoxypolytrimethoxysilane usually in an amount of 0.2% to 1.0% by weight based on the weight of the binder composition.

The following Examples will serve to illustrate the invention:-

EXAMPLE 1

A resol phenol-formaldehyde resin was synthesised having the following composition:-

|                          |         |
|--------------------------|---------|
| phenol                   | 800.00g |
| 91% W/W paraformaldehyde | 642.20g |



|                                   |          |
|-----------------------------------|----------|
| 50% W/W sodium hydroxide solution | 40.85g   |
| F:P molar ratio                   | 2.3:1    |
| OH :P molar ratio                 | 0.06:1   |
| Water in starting composition     | 5.2% W/W |

The following procedure was used:-

1. Charge and melt phenol
2. Charge paraformaldehyde and part of the sodium hydroxide solution and heat to 60 - 65°C at a ~~rate~~ of 1°C per minute
3. Cool to counteract exothermic reaction and maintain at 60 - 65°C while adding the remainder of the sodium hydroxide solution over a period of 1 hour
4. Heat to 75°C at a rate of 1°C per minute
5. Maintain at 75°C for 30 minutes
6. Heat to 85°C at a rate of 1°C per minute
7. Maintain at 85°C for sufficient time for the resin to reach a viscosity of 4000 - 6000 cp at 25°C as measured on a 25g sample diluted with 15g of 50% w/w potassium hydroxide solution using Paint Research Association Bubble Viscosity Tubes.

The resin was used to produce a base binder (1) having the following composition by weight:-

|                                      |             |
|--------------------------------------|-------------|
| resin                                | 25.00 parts |
| 50% W/W potassium hydroxide solution | 35.00 parts |
| borax                                | 5.50 parts  |
| gamma aminopropyltriethoxysilane     | 0.39 parts  |

The potassium hydroxide solution was added to the resin, the temperature rise due to exothermic reaction was controlled and the resin was cooled. The borax was added and mixed into the resin until it had dissolved. The silane was then added at a temperature of below



30°C. The molar ratio of alkali to phenol in the base binder was approximately 2:1.

Binder composition 2 was prepared from some of the base binder 1 by dissolving 2% by weight of pure phenyl monoethylene glycol monoether in 98% by weight of base binder 1.

Both binders were tested as binders for foundry sand using the following procedure:-

3% by weight of the binder based on the weight of sand was mixed with Chelford 60 sand (AFS Fineness No. 62) and the mixture was used to prepare standard AFS 50 mm X 50 mm diameter cylindrical cores. The sand temperature was 18°C. The cores were hardened by the passage of carbon dioxide gas for various times at 0.35kg/cm<sup>2</sup> line pressure and a 6.0 litres per minute flow rate.

Some of the cores were tested immediately after gassing on a George Fischer Universal Strength Machine Type PFA fitted with a High-Dry Compressive Strength Attachment Type PHD. Some were tested after storage for 3 days in dry storage conditions (temperature 17 - 20°C, relative humidity 30 - 35%) and others were tested after storage for 3 days in humid storage conditions (temperature 26 - 28°C, relative humidity 85 - 90%).

The results obtained are tabulated in Table 1 below.



| COMPRESSION STRENGTH (kg/cm <sup>2</sup> ) |      |      |      |
|--|------|------|------|
| BINDER                                     |      | 1    | 2    |
| <u>AS GASSED</u>                           |      |      |      |
| GASSING TIME                               | 30S  | 12.9 | 19.5 |
|  | 60S  | 15.5 | 22.1 |
|  | 120S | 18.3 | 24.3 |
| <u>DRY STORAGE</u>                         |      |      |      |
| GASSING TIME                               | 30S  | 17.0 | 26.4 |
|  | 60S  | 16.4 | 23.0 |
|  | 120S | 16.5 | 27.5 |
| <u>HUMID STORAGE</u>                       |      |      |      |
| GASSING TIME                               | 30S  | 13.4 | 22.1 |
|  | 60S  | 14.0 | 22.7 |
|  | 120S | 14.1 | 22.1 |

TABLE 1



EXAMPLE 2

Using some of the basic binder 1 of Example 1 a binder composition 3 was prepared by dissolving 5% by weight of pure phenyl monoethylene glycol monoether in 95% by weight of base binder 1.

Binders 1 and 3 were tested as described in example 1 except that for the storage tests the test cores were stored for 24 hours instead of 3 days.

The results obtained are tabulated in Table 2 below.



| COMPRESSION STRENGTH (kg/cm <sup>2</sup> ) |      |      |      |
|--|------|------|------|
| BINDER                                     |      | 1    | 3    |
| <u>AS GASSED</u>                           |      |      |      |
| GASSING TIME                               | 30S  | 12.9 | 19.3 |
|  | 60S  | 17.2 | 22.3 |
|  | 120S | 18.2 | 24.9 |
| <u>DRY STORAGE</u>                         |      |      |      |
| GASSING TIME                               | 30S  | 18.0 | 29.0 |
|  | 60S  | 20.5 | 31.0 |
|  | 120S | 20.7 | 29.6 |
| <u>HUMID STORAGE</u>                       |      |      |      |
| GASSING TIME                               | 30S  | 14.0 | 25.1 |
|  | 60S  | 15.6 | 24.2 |
|  | 120S | 15.6 | 24.4 |

TABLE 2



EXAMPLE 3

A series of binders 4 - 7 were prepared from base binder 1 containing respectively 2%, 4%, 7.5% and 10% by weight of pure phenyl monoethylene glycol monoether (PMEGE) based on the weight of the binder.

The binders were tested using the same procedure as described in Example 1. The sand temperature was 18 - 18.5°C, the dry storage conditions were 17 - 19°C, and 40 - 45% relative humidity and the humid storage conditions were 25 - 27°C and 80 - 90% relative humidity.

The results obtained are tabulated in Tables 3, 4, and 5 below.

| BINDER | P M E G E<br>(WT%) | COMPRESSION STRENGTH (kg/cm <sup>2</sup> ) AS<br>GASSED FOR GASSING TIME |      |      |
|--------|--------------------|--|------|------|
|        |                    | 30S  | 60S  | 120S |
| 4      | 2.0                | 15.5   | 18.8 | 19.8 |
| 5      | 4.0                | 16.0   | 19.3 | 20.7 |
| 6      | 7.5                | 14.4   | 17.8 | 19.7 |
| 7      | 10.0               | 13.5   | 16.1 | 19.0 |

TABLE 3



| BINDER | P M E G E<br>(WT%) | COMPRESSION STRENGTH (kg/cm <sup>2</sup> )<br>AFTER DRY STORAGE FOR GASSING<br>TIME |      |      |
|--------|--------------------|---|------|------|
|        |                    | 30S   | 60S  | 120S |
| 4      | 2.0                | 27.6  | 29.0 | 29.0 |
| 5      | 4.0                | 33.0  | 35.0 | 35.5 |
| 6      | 7.5                | 33.5  | 39.0 | 35.0 |
| 7      | 10.0               | 33.5  | 36.0 | 36.5 |

TABLE 4

| BINDER | P M E G E<br>(WT%) | COMPRESSION STRENGTH (kg/cm <sup>2</sup> )<br>AFTER HUMID STORAGE FOR GASSING<br>TIME |      |      |
|--------|--------------------|---|------|------|
|        |                    | 30S   | 60S  | 120S |
| 4      | 2.0                | 20.6  | 19.6 | 21.4 |
| 5      | 4.0                | 22.9  | 23.0 | 23.9 |
| 6      | 7.5                | 35.6  | 29.2 | 28.6 |
| 7      | 10.0               | 27.0  | 29.5 | 28.9 |

TABLE 5

The results in the Examples demonstrate the benefit of adding phenyl monoethylene glycol monoether to the base resin in terms of core strength. As gassed strength of the cores tends to peak at about 4% by weight addition while storage strengths continue to show improvements at higher levels of addition.



CLAIMS

1. A binder composition comprising an alkaline aqueous solution of a resol phenol-aldehyde resin and an oxyanion which can form a stable complex with the resin, the amount of alkali present in the solution is sufficient to substantially prevent stable complex formation between the resin and the oxyanion, wherein the molar ratio of alkali to phenol is from 1.5:1 to 2.5:1 and the binder composition also contains phenyl monoethylene glycol monoether.
2. A binder composition according to Claim 1 wherein the phenyl monoethylene glycol monoether is the pure compound or a mixture of phenyl monoethylene glycol monoether and phenol diethylene glycol ether.
3. A binder composition according to Claim 1 or Claim 2 wherein the phenyl monoethylene glycol monoether is present in an amount of 1% to 10% by weight based on the weight of the binder composition.
4. A binder composition according to Claim 3 wherein the phenyl monoethylene glycol monoether is present in an amount of 2% to 5% by weight based on the weight of the binder composition.
5. A binder composition according to any one of Claims 1 to 4 wherein the composition contains in addition a silane.
6. A binder composition according to Claim 5 wherein the silane is gammaaminopropyltrimethoxysilane, N-(2-aminoethyl)-3-aminopropyltrimethoxysilane, phenol trimethoxysilane or gammaglycidoxypropyltrimethoxysilane.
7. A binder composition according to Claim 5 wherein the amount of silane present is from 0.25% to 1.0% by weight based on the weight of the binder composition.



8. A binder composition as claimed in Claim 1 substantially as herein described with reference to the Examples.
9. A process for the production of an article of bonded particulate material comprising forming to the desired shape a mixture of particulate material and a binder composition comprising an alkaline aqueous solution of a resol phenol-aldehyde resin having an alkali to phenol molar ratio of from 1.5:1 to 2.5:1, an oxyanion which can form a stable complex with the resin, and phenyl monoethylene glycol monoether, and passing carbon dioxide gas through the formed shape so as to cause the oxyanion to form a stable complex with the resin, and thereby to cure the resin.
10. A process for the production of an article of bonded particulate material as claimed in Claim 9 substantially as herein described with reference to the Examples.

DATED this 8th December 1993

FOSECO INTERNATIONAL LIMITED

By its Patent Attorneys

GRIFFITH HACK & Co.



## A B S T R A C T

A binder composition comprising an alkaline aqueous solution of a resol phenol-aldehyde resin and an oxyanion which can form a stable complex with the resin, the amount of alkali present in the solution being sufficient to substantially prevent stable complex formation between the resin and the oxyanion, wherein the molar ratio of alkali to phenol is from 1.5:1 to 2.5:1 and the binder composition also contains a phenyl ethylene glycol ether.