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(54) **Foundry binder system with low emission of aromatic hydrocarbons**

Giessereibindemittelsysteme mit niedriger Emission von aromatischen Kohlenwasserstoffen

Liants pour la fonderie avec émission faible d'hydrocarbures aromatiques

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- **PATENT ABSTRACTS OF JAPAN vol. 1999, no. 09, 30 July 1999 (1999-07-30) & JP 11 090580 A (KAO CORP), 6 April 1999 (1999-04-06)**
- **DATABASE WPI Section Ch, Week 197737 Derwent Publications Ltd., London, GB; Class E17, AN 1977-66042Y XP002318113 & JP 52 093714 A (MUSASHINO KAGAKU KE) 6 August 1977 (1977-08-06)**

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Description

[0001] The present invention relates to furan resin-based binder systems to be used as binders mixed with sand or similar granular substances for the production of moulds or cores for use in foundries.

STATE OF THE ART

[0002] The above-mentioned binder systems for foundries normally consist of two or more components which are mixed with sand or similar granular substances so as then to form the cores or moulds around which or into which the molten metal will then be poured.

[0003] Typical binder systems are those of the polyurethane type, for example, normally consisting of a hydroxyl component, a polyisocyanate and a catalyst. Such binder systems are described in the following documents, for example: US-3,409,579; US-3,676,392; US-3,485,797; WO 97/05447 and WO 00/40351.

[0004] Widespread adoption of no-bake furan binder systems dates from the 1960's and they are still used extensively, being described, for example, on pages 30-34 of the publication "No-bake core & molds" issued in 1980 by the American Foundrymen's Society, incorporated here for reference purposes. These binder systems consist of two liquids (furan resin and acid hardener) which, added to the sand, produce without the use of heat cores and moulds suitable for the production of ferrous and nonferrous metal castings.

[0005] Furan resin consists substantially of furfuryl alcohol condensed to a greater or lesser degree with formaldehyde, modified where appropriate with urea, phenolic resins and various additives; furan resins which can be used in binder systems of the no-bake type are described, for example, on pages B320-6 to B320-15 of the publication "Manual of chemically setting sands", issued by the Centre Technique des Industries de la Fonderie in 1993, incorporated here for reference purposes.

[0006] The acid hardener generally consists of one or more sulphonic acids in aqueous or hydroalcohol solutions and contains varying amounts of sulphuric acid.

[0007] The sulphonic acids most frequently used are benzenesulphonic acid, toluenesulphonic acid, xylenesulphonic acid and cumenesulphonic acid. Of these, toluenesulphonic acid is by far the most widely used.

[0008] Sulphuric acid, generally present in small amounts in sulphonic acids as a residue of the sulphonation process, is in some cases added intentionally in very large amounts to the hardener to increase the acid energy and therefore accelerate the reaction of hardening of the binder system.

[0009] The hardeners just described, coming into contact with the molten metal during casting, break down releasing aromatic hydrocarbons and sulphurous anhydride. This phenomenon has been monitored by BCIRA (British Cast Iron Research Association), which as early as 1981 published the experimental data collected in the report "Environmental pollution arising from cold-setting sands catalysed by different sulphonic acids".

[0010] The report shows that the sulphonic acids evolve not only the aromatic hydrocarbon from which they are derived (for example toluene in the case of toluenesulphonic acid) but also undergo partial dealkylation of the aromatic ring with the formation of benzene. For benzene, classified as a "recognized human carcinogen", the limits in force for concentrations in the workplace and for emissions into the atmosphere are far more restrictive than those of the other aromatic hydrocarbons.

[0011] Foundries are therefore faced with the problem of not exceeding benzene emission limits, a problem which is not easy to solve since bringing down the benzene contained in the air is much more complex than bringing down the sulphurous anhydride, for example.

[0012] JP 11 09058 discloses a curing agent composition for casting mold capable of reducing the content of sulfonic acid.

DESCRIPTION OF THE INVENTION

[0013] The invention on which the present patent application is based addresses and solves the problem just described with a binder system for foundry sands which can be used in processes of the no-bake type consisting of a furan resin and an acid hardener in which the arylsulphonic acid is completely replaced by an aliphatic acid and by sulphuric acid.

[0014] Since the simpler aliphatic carboxylic acids (formic acid, acetic acid, propionic acid) are not usable in practice because of their pungent or unpleasant odour, the invention provides for the use of aliphatic hydroxy acids and in particular of 2-hydroxypropionic acid (lactic acid) and/or of 2-hydroxypropane-1,2,3-tricarboxylic acid (citric acid).

[0015] As with the conventional hardeners described in the introduction, the presence of sulphuric acid serves to increase the acid energy of the hardener which is the subject of the present invention.

[0016] The hardener which is the subject of the invention, coming into contact with the molten metal, does not evolve aromatic hydrocarbons or evolves a reduced amount of them, depending on the quantity of arylsulphonic acid which it may contain.

[0017] The acid hardeners which are the subject of the present invention have the following composition by weight:

a)	water	10-50%
b)	sulphuric acid	0.5-40%
c)	aliphatic hydroxy acid	10-60%

where the sum of the percentages of components a), b) and c) is 100 and the components are assumed to be pure.

[0018] Preferably, the water content is between 25 and 50% by weight, the sulphuric acid content is between 10 and 35% by weight and the aliphatic hydroxy acid content is between 20 and 50% by weight; according to a preferred aspect, the aliphatic hydroxy acid content is greater than 20% by weight and in any case not less than 22%.

[0019] Arylsulphonic acid is absent.

[0020] According to a preferred aspect of the invention, the aliphatic hydroxy acid is selected from lactic acid and/or citric acid; arylsulphonic acid.

[0021] The hardener which is the subject of the invention is mixed with the sand together with the furan resin at ambient temperature to give the cores and moulds suitable for the production of ferrous and nonferrous metal castings; preferably, 100 parts by weight of silica sand or other refractory material are mixed with 0.2-0.8, preferably approximately 0.4-0.6 parts by weight of acid hardener and with 0.6-1.5, preferably 0.8-1.2 parts by weight of furan resin.

[0022] By the term ambient temperature is meant a temperature between roughly 0° and +40° C, preferably between +15 and +30° C, depending on the geographical position (latitude, altitude etc.) in which the foundry is situated.

[0023] The furan resins which are preferably used in the embodiment of the present invention are those already described on pages 30-34 of the publication "No-bake core & molds" already cited and on pages B320-6 to B320-15 of the "Manual of chemically setting sands" already cited, both incorporated here for reference purposes.

[0024] Preferably, the furan resin will have a content by weight of furfuryl alcohol of 60-80%, a nitrogen content of 1-8% and a water content of 5-20%; particularly preferred is a furan resin containing approximately 75% by weight of furfuryl alcohol, approximately 10% of urea-formaldehyde resin (corresponding to about 2% of nitrogen) and about 15% of water.

[0025] These and other aspects of the invention will become clear from the following examples provided purely by way of non-limiting examples of the invention.

Examples

[0026]

Note 1: the percentages indicated in the examples are by weight.
Note 2: the components used for the examples have the following characteristics:

- the 62% sulphuric acid is commercial 50° Bé sulphuric acid (approximately 62%);
- the 80% lactic acid is a commercial aqueous solution, approximately 80%;
- the monohydrate citric acid is commercial monohydrate citric acid;
- the 65% toluenesulphonic acid is an aqueous solution containing 65% of toluenesulphonic acid with prevalence of the para isomer and approximately 1.2% of sulphuric acid, marketed for example by Cavenaghi SPA with the designation "H 60 hardener";

Hardener 1 (according to the invention)

[0027]

Sulphuric acid	62%	40%
Lactic acid	80%	60%
Total		100

Hardener 2 (according to the invention)

[0028]

Water	25%

(continued)

Monohydrate citric acid	25%
Sulphuric acid 62%	50%
Total	100

Hardener 3 (for comparison)

[0029]

Sulphuric acid 62%	40%
Lactic acid 80%	30%
Toluenesulphonic acid 65%	30%
Total	100

Hardener 4 (for comparison)

[0030]

Water	25%
Monohydrate citric acid	25%
Sulphuric acid 62%	30%
Toluenesulphonic acid 65%	20%
Total	100

Hardener 5 (for comparison)

Toluenesulphonic acid 65% 100%

[0031]

Control mixture

100	parts by weight	silica sand LA32
0.4	parts by weight	hardener
1.0	parts by weight	GIOCA NB 2F resin

[0032] GIOCA NB 2F resin is the commercial designation of a furan resin obtained by condensation of furfuryl alcohol, formaldehyde and urea, marketed by Cavenaghi SPA.

[0033] This resin has the following composition:

- furfuryl alcohol approximately 75%
- nitrogen approximately 2%
- water approximately 15%

[0034] Standard +GF bars were prepared with the above-mentioned mixtures. The flexural strength of these bars was measured after 3, 5 and 24 hours from the time of discharging the mixture from the mixer; the results obtained are given in the following table:

Hardener	Setting		Flexural strength in kg/cm^2 after		
	Start	Finish	3 hours	5 hours	24 hours
1	30’	49’	9	17	23
2	18’	29’	9	11	16
3	17’	29’	14	16	17

(continued)

Hardener	Setting		Flexural strength in kg/cm^2 after		
	Start	Finish	3 hours	5 hours	24 hours
4	25'	37'	13	17	19
5	17'	23'	20	23	25

[0035] The results obtained demonstrate that, as well as offering the benefits claimed, the hardeners according to the invention also offer performance characteristics comparable with those of the control hardeners.

Claims

1. A no-bake foundry binder system composed of a furan resin and an acid hardener having the following composition by weight:

a)	water	10-50%
b)	sulphuric acid	0.5-40%
c)	aliphatic hydroxy acid	10-60%

where the sum of the percentages of components a), b), and c) is 100.

2. A binder system according to claim 1 **characterized in that** the water content of said acid hardner is between 25 and 50% by weight.

3. A binder system according to any one of the preceding claims **characterized in that** the sulphuric acid content of said acid hardner is between 10 and 35% by weight.

4. A binder system according to any one of the preceding claims **characterized in that** the aliphatic hydroxy acid content of said acid hardner is between 20 and 50% by weight.

5. A binder system according to any one of the preceding claims **characterized in that** the aliphatic hydroxy acid content of said acid hardner is greater than 20% by weight.

6. A binder system according to any one of the preceding claims **characterized in that** the aliphatic hydroxy acid content of said acid hardner is not less than 22% by weight.

7. A binder system according to any one of the preceding claims **characterized in that** said aliphatic hydroxy acid is selected from lactic acid and/or citric acid.

8. A binder system according to claim 1 composed of 0.2-0.8 parts by weight of said acid hardener and 0.6-1.5 parts by weight of furan resin.

9. A binder system according to claim 8 composed of approximately 0.4-0.6 parts by weight of said acid hardener and approximately 0.8-1.2 parts by weight of furan resin.

10. A binder system according to claims 8-9 **characterized in that** the furan resin has a furfuryl alcohol content of 60-80% by weight, a nitrogen content of 1-8% by weight and a water content of 5-20% by weight.

11. Foundry cores and/or moulds containing 0.2-0.8 parts by weight of an acid hardener, 0.6-1.5 parts by weight of furan resin and 80-120 parts by weight of sand or other refractory material, said acid hardener having the following composition by weight:

a)	water	10-50%
b)	sulphuric acid	0.5-40%

(continued)

c)	aliphatic hydroxy acid	10-60%

where the sum of the-percentages of components a), b), and c) is 100.

12. Cores and/or moulds according to claim 11 containing approximately 100 parts by weight of sand or other refractory material, approximately 0.4-0.6 parts by weight of said acid hardener and approximately 0.8-1.2% parts by weight of furan resin.

13. A method for the production of foundry cores and/or moulds **characterized in that** an acid hardener is mixed with sand or other refractory material at ambient temperature together with a furan resin, said acid hardener having the following composition by weight:

a)	water	10-50%
b)	sulphuric acid	0.5-40%
c)	aliphatic hydroxy acid	10-60%

where the sum of the percentages of components a), b), and c) is 100.

14. A method according to claim 13 **characterized in that** 80-120 parts by weight of sand are mixed with 0.2-0.8% parts by weight of said acid hardener and with 0.6-1.5 parts by weight of furan resin.

15. A method according to claim 14 **characterized in that** approximately 100 parts by weight of sand or other refractory material are mixed with approximately 0.4-0.6 parts by weight of said acid hardener and approximately 0.8-1.2 parts by weight of furan resin.

16. Foundry cores and/or moulds obtainable according to the process in claims 13-15.

Patentansprüche

1. Ein no-bake (ohne Backen) Gießereibindemittelsystem gebildet aus Furanharz und einem Säurehärter mit folgender Gewichtszusammensetzung:

a)	Wasser	10-50%
b)	Schwefelsäure	0,5-40%
c)	aliphatische Hydroxysäure	10-60%

wobei die Summe der Prozente der Bestandteile a), b) und c) 100 beträgt.

2. Bindemittelsystem gemäß Anspruch 1, **dadurch gekennzeichnet, dass** der Wassergehalt des genannten Säurehärters zwischen 25 und 50 Gew.-% liegt.

3. Bindemittelsystem gemäß einem der vorangehenden Ansprüche, **dadurch** gekenntzeichnet, dass der Schwefelsäuregehalt des genannten Säurehärters zwischen 10 und 35 Gew.-% liegt.

4. Bindemittelsystem gemäß einem der vorangehenden Ansprüche, **dadurch** gekenntzeichnet, dass der Gehalt an aliphatischer Hydroxysäure des genannten Säurehärters zwischen 20 und 50 Gew.-% liegt.

5. Bindemittelsystem gemäß einem der vorangehenden Ansprüche, **dadurch gekennzeichnet, dass** der Gehalt an aliphatischer Hydroxysäure des genannten Säurehärters größer als 20 Gew.-% ist.

6. Bindemittelsystem gemäß einem der vorangehenden Ansprüche, **dadurch gekennzeichnet dass** der Gehalt an aliphatischer Hydroxysäure des genannten Säurehärters nicht weniger als 22 Gew.-% ist.

7. Bindemittelsystem gemäß einem der vorangehenden Anspruche, **dadurch gekennzeichnet, dass** die genannte aliphatische Hydroxysäure aus Milchsäure und/oder Zitronensäure ausgewählt wird.

8. Bindemittelsystem gemäß Anspruch 1, gebildet aus 0,2-0,8 Gewichtsteilen des genannten Säurehärters und 0,6-1,5 Gewichtsteilen Furanharz.

9. Bindemittelsystem gemäß Anspruch 8, gebildet aus ungefähr 0,4-0,6 Gewichtsteilen des genannten Säurehärters und ungefähr 0,8-1,2 Gewichtsteilen Furanharz.

10. Bindemittelsystem gemäß einem der Ansprüche 8-9, **dadurch gekennzeichnet, dass** der Furanharz einen Furfurylalkoholgehalt von 60-80 Gew.-%, einen Stickstoffgehalt von 1-8 Gew.-% und einen Wassergehalt von 5-20 Gew.-% aufweist.

11. Gießkerne und/oder Gussformen enthaltend 0,2-0,8 Gewichtsteile Säurehärter, 0,6-1,5 Gewichtsteile Furanharz und 80-120 Gewichtsteile Sand oder anderes feuerfestes Material, wobei der genannte Säurehärter folgende Gewichtszusammensetzung aufweist:

a)	Wasser	10-50%
b)	Schwefelsäure	0,5-40%
c)	aliphatische Hydroxysäure	10-60%

wobei die Summe der Prozente der Bestandteile a), b) und c) 100 beträgt.

12. Kerne und/oder Formen gemäß Anspruch 11, enthaltend ungefähr 100 Gewichststeile Sand oder anderes feuerfestes Material, ungefähr 0,4-0,6 Gewichtsteile des genannten Säurehärters und ungefähr 0,8-1,2% Gewichtsteile Furanharz.

13. Ein Verfahren zur Herstellung von Gießkernen und/oder Gussformen, **dadurch gekennzeichnet, dass** der Säurehärter bei Raumtemperatur mit Sand oder anderem feuerfesten Material und zusammen mit Furanharz vermischt wird, wobei der genannte Säurehärter folgende Gewichtszusammensetzung aufweist:

a)	Wasser	10-50%
b)	Schwefelsäure	0,5-40%
c)	aliphatische Hydroxysäure	10-60%

wobei die Summe der Prozente der Bestandteile a), b) und c) 100 beträgt.

14. Verfahren gemäß Anspruch 13, **dadurch gekennzeichnet, dass** 80-120 Gewichtsteile Sand mit 0,2-0,8% Gewichtsteile des genannten Säurehärters und mit 0,6-1,5 Gewichtsteilen Furanharz vermischt werden.

15. Verfahren gemäß Anspruch 14, **dadurch gekennzeichnet, dass** ungefähr 100 Gewichtsteile Sand oder eines anderen feuerfesten Materials mit ungefähr 0,4-0,6 Gewichtsteilen des genannten Säurehärters und ungefähr 0,8-1,2 Gewichtsteilen Furanharz vermischt werden.

16. Gießkerne und/oder Gussformen, herstellbar mit einem der Verfahren gemäß Ansprüchen 13-15.

Revendications

1. Système de liants de fonderie sans cuisson, composé d'une résine de furane et d'un durcisseur acide ayant la composition en poids suivante :

a)	eau	10 à 50%
b)	acide sulfurique	0,5 à 40 %
c)	acide hydroxyaliphatique	10 à 60 %

la somme des pourcentages des composants a), b) et c) étant de 100.

2. Système de liants selon la revendication 1, **caractérisé en ce que** la teneur en eau dudit durcisseur acide est de 25 à 50 % en poids.

3. Système de liants selon l'une quelconque des revendications précédentes, **caractérisé en ce que** la teneur en acide sulfurique duditdit durcisseur acide est de 10 à 35 % en poids.

4. Système de liants selon l'une quelconque des revendications précédentes, **caractérisé en ce que** la teneur en acide hydroxyaliphatique dudit durcisseur acide est de 20 à 50 % en poids.

5. Système de liants selon l'une quelconque des revendications précédentes, **caractérisé en ce que** la teneur en acide hydroxyaliphatique dudit durcisseur acide est supérieure à 20 % en poids.

6. Système de liants selon l'une quelconque des revendications précédentes, **caractérisé en ce que** la teneur en acide hydroxyaliphatique dudit durcisseur acide n'est pas inférieure à 22 % en poids.

7. Système de liants selon l'une quelconque des revendications précédentes, **caractérisé en ce que** ledit acide hydroxyaliphatique est choisi parmi l'acide lactique et/ou l'acide citrique.

8. Système de liants selon la revendication 1, composé de 0,2 à 0,8 parties en poids dudit durcisseur acide et 0,6 à 1,5 parties en poids de résine de furane.

9. Système de liants selon la revendication 8, composé d'environ 0,4 à 0,6 parties en poids dudit durcisseur acide et d'environ 0,8 à 1,2 parties en poids de résine de furane.

10. Système de liants selon les revendications 8 et 9, **caractérisé en ce que** la résine de furane a une teneur en alcool de furfuryle de 60 à 80 % en poids, une teneur en azote de 1 à 8 % en poids et une teneur en eau de 5 à 20 % en poids.

11. Noyaux et/ou moules de fonderie contenant 0,2 à 0,8 parties en poids d'un durcisseur acide, 0,6 à 1,5 parties en poids de résine de furane et 80 à 120 parties en poids de sable ou d'un autre matériau réfractaire, ledit durcisseur acide ayant la composition en poids suivante :

a)	eau	10 à 50 %
b)	acide sulfurique	0,5 à 40 %
c)	acide hydroxyaliphatique	10 à 60 %,

la somme des pourcentages des composants a), b) et c) étant de 100.

12. Noyaux et/ou moules selon la revendication 11, contenant environ 100 parties en poids de sable ou d'un autre matériau réfractaire, environ 0,4 à 0,6 parties en poids dudit durcisseur acide et environ 0,8 à 1,2 parties en poids de résine de furane.

13. Procédé pour la production de noyaux et/ou de moules de fonderie, **caractérise en ce qu'**un durcisseur acide est mélangé à du sable ou à un autre matériau réfractaire à température ambiante conjointement avec une résine de furane, ledit durcisseur acide ayant la composition en poids suivante :

a)	eau	10 à 50 %
b)	acide sulfurique	0,5 à 40 %
c)	acide hydroxyaliphatique	10 à 60 %,

la somme des pourcentages des composants a), b) et c) étant de 100.

14. Procédé selon la revendication 13, **caractérisé en ce que** 80 à 120 parties en poids de sable sont mélangées à 0,2 à départies en poids dudit durcisseur acide et à 0,6 à 1,5 parties en poids de résine de furane.

15. Procédé selon la revendication 14, **caractérisé en ce qu'**environ 100 parties en poids de sable ou d'un autre matériau réfractaire sont mélangées à environ 0,4 à 0,6 parties en poids dudit durcisseur acide et à environ 0,8 à 1,2 parties en poids de résine de furane.

16. Noyaux et/ou moules de fonderie pouvant être obtenus selon le procédé des revendications 13 à 15.

REFERENCES CITED IN THE DESCRIPTION

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