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(21) International Application Number: PCT/GB93/01792 (22) International Filing Date: 23 August 1993 (23.08.93) (30) Priority data: 9218596.6 2 September 1992 (02.09.92) GB (71) Applicant (for all designated States except US): ASHLAND CHEMICAL LIMITED [GB/GB]; Vale Industrial Estate, Kidderminster, Worcestershire DY11 7QP (GB). (72) Inventors; and (75) Inventors/Applicants (for US only): BUSBY, Andrew, David [GB/GB]; 493 Chester Road South, Kidderminster, Worcestershire DY10 1XD (GB). VERNON, Philip [GB/GB]; 3 Ludlow Road, The Poplars, Kidderminster, Worcestershire DY10 1NR (GB).		(74) Agent: RACKHAM, Anthony, Charles; Lloyd Wise, Tregear & Co., Norman House, 105-109 Strand, London WC2R OAE (GB). (81) Designated States: AT, AU, BB, BG, BR, BY, CA, CH, CZ, DE, DK, ES, FI, GB, HU, JP, KP, KR, KZ, LK, LU, MG, MN, MW, NL, NO, NZ, PL, PT, RO, RU, SD, SE, SK, UA, US, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i>
(54) Title: RECLAMATION OF ESTER-CURED PHENOLIC RESIN BONDED FOUNDRY SANDS (57) Abstract Attrition reclaimed ester-cured phenolic resin bonded sand is subject to thermal treatment prior to re-use. Prior to the thermal treatment, however, the attrition reclaimed sand is contacted with an additive which converts potassium compounds to a form having a melting point of at least 550 °C and the thermal treatment is effected at a temperature below that at which the resulting potassium compound fuses.		

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**Reclamation of Ester-Cured Phenolic
Resin Bonded Foundry Sands**

This invention relates to the reclamation of foundry sands from used foundry moulds which have been fabricated by bonding foundry sand with ester-cured phenolic resin binders.

5 There is an increasing demand to recycle foundry
sands from moulds after casting. The demand is fuelled not
only by the cost of virgin sand but also by the problems
associated with the disposal of the used resin coated sand.
In the past such material was readily disposed of in land
fill sites but recently the authorities have become more
10 environmentally conscious and in many regions there are
strict regulations governing the disposal of such materials.

One known method of sand reclamation comprises
attrition of the bonded sand to break up the agglomerates
into individual particles. Whilst the attrition process may
15 remove some resin from the sand particles by abrasion which
will be removed with the fines, resin remains on the surface
of sand particles and the re-bonding properties of the
attrition reclaimed sand are inferior to the bonding
properties of new sand. Generally, conventional attrition
20 techniques allow re-use of up to 85% of the resin bonded
sand, the remaining sand being dumped.

Known thermal techniques for reclaiming foundry sand
after attrition comprise heating the sand in a fluidised bed
to a sufficiently high temperature to remove the organic

resin effectively and to ensure low emissions from the exhaust gas. However, it has been found that such a thermal reclamation process is not particularly successful with ester-cured bonded foundry sands because there is a tendency
5 for the sand grains to agglomerate in the thermal reclaimer preventing efficient operation of the fluidised bed at temperatures high enough to remove the binder effectively and ensure low emissions. At low temperatures there is inefficient removal of the resin. Sand reclaimed by the
10 known thermal techniques exhibits re-bonding properties inferior to new sand and comparable to sand reclaimed by attrition.

It is believed the problem of agglomeration in the thermal reclamation system is due to the presence of
15 potassium in the resin binder system which is generally in the form of potassium hydroxide and associated ester salts. It is postulated that the potassium compounds decompose and/or melt during the thermal treatment which results in agglomeration of sand particles, the particles being bonded
20 or attracted to each other to such an extent that the fluidising gas is unable to maintain an effective fluidised bed.

The potassium compounds could be removed by washing the foundry sand prior to thermal treatment. However, such
25 washing would significantly increase the energy requirements

to dry and thermally treat the washed sand that such a procedure would be uneconomic.

It is an object of the present invention to provide an improved reclamation process for ester-cured phenolic bonded foundry sands.

Therefore according to the present invention there is provided a process comprising the thermal treatment of attrition reclaimed ester-cured phenolic resin bonded sand in which prior to the thermal treatment the attrition reclaimed sand is contacted with an additive which converts potassium compounds to a form having a melting point of at least 600°C and the thermal treatment is effected at a temperature below that at which the resulting potassium compound fuses.

It has been found that by converting the potassium hydroxide and other salts in the ester-cured resin system to a potassium compound having a melting point above 550°C, and preferably above 700°C, the sand can be thermally processed at sufficiently high temperatures to remove the resin coating effectively and ensure low emissions but without agglomeration of the sand. Furthermore, there is a significant reduction in the potassium content of the coated sand after the thermal treatment and the resulting sand exhibits rebonding properties superior to attrition reclaimed sand and often comparable to new sand. The process also

allows recycling of more sand than with conventional techniques.

There are a number of potassium compounds having a melting point above 550°C including the antimonide (812°C),
5 metaborate (947°C), chloride (776°C), chromate (975°C), fluoride (880°C), iodide (723°C), molybdate (919°C), ortho-phosphate (1340°C), metaphosphate (807°C), silicate (976°C) and sulphate (1069°C), bromide (730°C) and carbonate (891°C).

According to one preferred embodiment of the
10 invention, the additive is in the form of an aqueous solution of a compound which will react with potassium hydroxide to yield such a potassium compound. Suitable acid or salt solutions for use as an additive include halogen acids, e.g. HCl, HBr, HI, sulphuric acid, boric acid, and ammonium salts
15 of such acids such as, ammonium chloride.

However we have found that the additive need not necessarily be added as a solution. Some possible additives are not really soluble and additionally in some circumstances it may be advantageous to use completely dry sand in the
20 thermal treatment step. In these cases it is possible to make the addition as a finely dispersed powdered solid. Examples are calcium compounds such as the sulphate and clays with a base exchange capability. Thus, calcium sulphate would convert the potassium compounds to potassium sulphate
25 of high melting point whilst the calcium oxides would form as

a fine powder which would disperse with the fines from the fluidising bed.

The amount of additive employed is preferably at least that required to convert all the potassium in the resin to the thermally stable form. In the case where the additive is added as an aqueous solution, the amount added will depend upon the concentration of the solution. Generally the amount of the additive will be at least 0.25% by weight of the sand and preferably from 0.5 to 5% by weight of the sand. When the additive is added as an aqueous solution the amount is generally selected to be sufficient to wet all the sand particles (at least about 0.25 to 0.5% by weight of the sand) but not in large amounts which would significantly increase the energy requirements for drying and thermally treating the sand. The maximum amount of aqueous additive is generally less than 5% by weight of sand. Preferably the aqueous additive is used in an amount of about 2.5% by weight of sand.

The aqueous solution of the additive may additionally include a surfactant, e.g. sodium salts of sulphated fatty alcohols, to improve the wetting of the sand particles.

The additive may be added to and mixed with the sand in a conventional mixer. Conveniently the additive may be mixed with the sand in the screw conveyor feeding a thermal reclaimer.

Thermal treatment may be conducted in any known type of thermal reclaimer employing any known heating technique. Generally reclaimers in which the sand is fluidised and heated, generally using a gas fired fluidised bed, are preferred. The sand is generally heated to a temperature in the range of 600°C to 1000°C, usually 700°C to 800°C, with a stack temperature of about 1100°C to ensure clean burning and low emissions. The dwell time in the thermal reclaimer may vary but adequate results have been obtained with a dwell time of 30 minutes.

The invention will now be illustrated by the following Examples according to the invention and Comparative Examples.

All the Examples and Comparative Examples employed attrition reclaimed sand taken from a commercial foundry. The sand contained residues of ester-cured alkaline phenolic resin, the original foundry binder comprising Novaset 720 phenolic resin and Novaset 6 Hardener (triacetin/ γ -butyrolactone 50:50) commercially available from Ashland Chemical Limited.

The thermal treatment was carried out in a Richards gas fired, fluidised bed thermal reclaimer having a throughput of about 300kg per hour. The residence time of sand in the thermal reclaimer was about 30 minutes.

Example 1

Attrition reclaimed sand was pre-mixed with 2.5% by weight of a 10% aqueous solution of hydrochloric acid in a continuous sand mixer screw-type conveyor and charged into the fluidised bed thermal reclaimer having an average bed temperature of 730°C.

Loss on ignition, potassium content and bonding tests were conducted on attrition reclaimed sand, thermally reclaimed sand and new sand. The bonding tests were conducted according to AFS Standard Compression Strength Test using Novaset 726 alkaline phenolic resin (1.5% by weight of sand) and Novaset 6 hardener (25% by weight of resin). The results are reported in the following Table.

	Attrition Reclaimed Sand	Thermally Reclaimed Sand	New Sand
Loss on ignition	1.8%	0.1%	0.2%
Potassium	0.12%	0.07%	0.01%
Compression Strengths (psi)			
1 hour	87	105	91
2 hours	105	178	164
4 hours	152	312	228
24 hours	163	392	440

The thermally reclaimed sand was analyzed for chloride ion content. This was found to be 0.05%. The stoichiometric ratio of potassium to chloride ions would be 1.1:1 for 100% KCl. On the basis of our results it would

appear that about 80% of the remaining potassium is present as the chloride.

It should be noted that the potassium analysis determines only "free" potassium and does not detect the potassium complexes known to be present within the mineral structure of new (virgin) sand.

Example 2

Adopting the same procedures as in Example 1 attrition reclaimed sand was pre-mixed with 2.5% by weight of a 10% aqueous solution of ammonium chloride. The sand was then charged into the fluidised bed thermal reclaimer with an average bed temperature of 730°C.

Results:-

	Attrition Reclaimed	Thermally Reclaimed	New Sand
Loss on ignition	1.8%	0.15%	0.2%
Potassium	0.12%	0.06%	0.01%
Compression Strengths (psi)			
1 hour	21	36	29
2 hours	54	80	72
4 hours	134	283	238
24 hours	235	420	460

Example 3 (Comparative)

Adopting the same procedures as in Example 1 2.5% of water containing a small addition of a wetting agent (surfactant) to facilitate wetting of the sand was mixed with the sand.

The sand was then charged into the fluidised bed thermal reclaimer with an average bed temperature of 730°C.

The attrition reclaimed sand with this additive was found to agglomerate in the thermal reclaimer. The
5 agglomerated mass within the reclaimer prevented normal discharge and terminated the test.

The sand was removed from the thermal reclaimer and found to be only loosely agglomerated at ambient temperatures. The potassium level of this reclaimed sand was
10 found to be very similar to the attrition sand and little benefit from this treatment was obtained. Re-bonding properties were identical to the attrition reclaimed sand.

Example 4 (Comparative)

This test involved charging the attrition reclaimed
15 sand without a prior addition in to the thermal reclaimer. The thermal reclaimer was run at the same conditions as previous tests.

The attrition reclaimed sand agglomerated in the thermal reclaimer and terminated the test as in Example 3.
20 The potassium level and re-bonding properties of the resulting sand was very similar to that of the attrition reclaimed sand.

Example 5

The procedures of Example 1 were repeated using hydrochloric acid of varying concentrations and other acids and differing reaction conditions. The details of the additive and reactor conditions are tabulated below:

	Run	Additive	Concentration of acid solution(%)	Rate of Addition (% by wt of sand)	Temperature (°C)
10	1	HCl	10	2	760
	2	HCl	10	2	850
	3	HCl	10	1	760
	4	H ₂ S ₁ F ₆	10	1	730
	5	HCl	10	2	750
15	6	HCl	28*	0.8	750
	7	H ₂ SO ₄	26†	0.7	750.

* Commercial Concentration

† Battery Acid Concentration

The resulting treated sands of Runs 1 to 4 were then tested as described in Example 1 and the results are set out below:

Attrition Sand (no additive)

Loss on ignition = 1.8%
Potassium = 0.12%

Run 1

Loss on ignition = 0.10%
Potassium = 0.07%
Chloride ion = 0.05%

5 Bonding strengths were not determined.

Run 2

Loss on ignition = 0.04%
Potassium = 0.07%
Chloride ion = 0.03%

10 The bed showed signs of sintering but did not block up. Sintering dispersed when the temperature was reduced to 760°C (note melting point of KCl is 776°C). Bonding strengths were not determined.

Run 3

15 Loss on ignition = 0.09%
Potassium = 0.11%
Chloride ion = 0.02%

Bonding strengths were not determined.

Run 4

20 Loss on ignition = 0.09%
Potassium = 0.10%
Fluoride ion = 0.008%

25 The treated sand of Run 4, the attrition sand noted above, and new sand were then subjected to bonding tests as described in Example 1 using the resin and hardener as described in Example 1. The resulting compression strengths (p.s.i.) are tabulated below:

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	<u>After (h)</u>	<u>New</u>	<u>Attrition</u>	<u>Thermal</u>
	1	262	90	287
	1	294	147	312
5	4	412	186	430
	24	586	202	603

As can be seen the sand treated according to the invention gave bonding strengths comparable to new sand and very much better than sand treated solely by attrition.

10 The resulting treated sands of Runs 5 to 7 were then tested as described in Example 1 except that for bonding Novaset 720 (1.5% by weight of sand) and (NH10S hardener (25% by weight of resin) were used. The results, as compared with sand subjected to attrition only and new sand are set out
15 below:

Attrition Only

Loss on Ignition = 1.45%
Potassium = 0.24%
Chloride ion = 0.0002%

20 Compression Strengths (p.s.i.)

After (h)	1	2	4	24
	131	174	203	268

New Sand

25 Loss on Ignition = 0.22%
Potassium = 0.01%

13

Compression Strengths (p.s.i.)

After (h)	1	2	4	24
	326	435	566	609

Run 5

5	Loss on Ignition	=	0.09%
	Potassium	=	0.10%
	Chloride ion	=	0.07%

Compression Strengths (p.s.i.)

After (h)	1	2	4	24
10	319	479	537	740

Run 6

	Loss on Ignition	=	0.08%
	Potassium	=	0.13%
	Chloride ion	=	0.06%

15 Compression Strengths (p.s.i.)

After (hr.)	1	2	4	24
	348	428	478	769

Run 7

20	Loss on Ignition	=	0.04%
	Potassium	=	0.17%
	Sulphur	=	0.06%

Compression Strengths (p.s.i.)

After (h)	1	2	4	24
	355	442	452	679

25 Example 6

Following a similar procedure to that of Example 5, attrition reclaimed sand was well mixed with 1% by weight of powdered calcium sulphate. The resulting mixture was then heated in the fluidised bed at a temperature of 750°C. The

sand did not agglomerate.

The resulting treated sand was then tested and bonding tests similar to those of Runs 5 to 7 of Example 6 were made. The results were as follows:

5 Loss on Ignition = 0.09%
 Potassium = 0.15%
 Sulphur = 0.08%

Compression Strengths (p.s.i.)

After (h)	1	2	4	24
10	168	298	347	463

These results, when compared with the results for new and attritioned sand tested in Example 5, show good improvements, although the bonding strengths were lower than when the addition was added in liquid form. Possibly the reason for this is the retention of calcium compounds in the sand.

These results demonstrate that the production of the thermally stable salt does appear to be the mechanism by which sintering is avoided. The potassium chloride appeared to sinter when the temperature was 850°C but not when the temperature was reduced to 760°C (see Run 2)

Also a wide range of concentrations and addition levels will enable the sand to be thermally reclaimed. Reducing the overall chloride level reduced the chloride ion content of the reclaimed sand, and resulted in a greater quantity of retained potassium. Similarly using a smaller addition of a more concentrated additive reduced salt

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production efficiency somewhat. However perfectly usable sand was produced.

Thus there should be sufficient addition to provide enough salt to avoid sintering, and preferably sufficient addition to wet the sand without too much excess water.

CLAIMS:

1. A process comprising the thermal treatment of attrition reclaimed ester-cured phenolic resin bonded sand characterised in that prior to the thermal treatment the
5 attrition reclaimed sand is contacted with an additive which converts potassium compounds to a form having a melting point of at least 550°C and the thermal treatment is effected at a temperature below that at which the resulting potassium compound fuses.
- 10 2. A process as claimed in Claim 1 in which the additive converts potassium compounds to a form having a melting point above 700°C.
3. A process as claimed in Claim 1 or Claim 2 in which the additive is contacted with the sand in the form of an
15 aqueous solution.
4. A process as claimed in any preceding claim in which the additive is selected from one or more of halogen acids, sulphuric acid, boric acid and ammonium salts of these acids.
5. A process as claimed in Claim 1 or Claim 2 in which
20 the additive is in the form of a powdered solid.
6. A process as claimed in Claim 5 in which the additive is a calcium compound.

7. A process as claimed in any preceding claim in which the additive is used in an amount of at least 0.25% by weight of the attrition reclaimed sand.

8. A process as claimed in any preceding claim in which the additive is used in an amount in the range from 0.5 to 5% by weight of attrition reclaimed sand.

9. A process as claimed in any preceding claim in which the thermal treatment is conducted at a temperature of 600 to 1000°C.

10. A process as claimed in Claim 9 in which the thermal treatment is conducted at a temperature of 700 to 800°C.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 93/01792

A. CLASSIFICATION OF SUBJECT MATTER
IPC 5 B22C5/00 B22C1/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 5 B22C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,Y	FOUNDRY TRADE JOURNAL vol. 167, no. 3478, 9 July 1993, REDHILL, SURREY, GB pages 391 - 393 XP372499 M J FALLON 'Prospects of reclaiming greensand for coremaking use' *page 391, paragraph "The influence of alkaline materials" *	1,3-6,9, 10
Y	DE,A,26 56 672 (DAIMLER-BENZ AG) 9 February 1978 see claims see column 2, line 32 - line 59 see figure	1,3-6,9, 10
A	GB,A,L20204 (POULSON ET AL) 3 October 1912 &GB-A-20204 A.D. 1911 see whole document	1,5,6

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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INTERNATIONAL SEARCH REPORT

Information on patent family members

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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
DE-A-2656672	09-02-78	NONE	
GB-A-L20204		NONE	