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3,050,797

WATER SENSITIVE MOLDS AND CORES OF FAST COLLAPSIBILITY

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No Drawing. Filed June 18, 1959, Ser. No. 821,084
6 Claims. (Cl. 22-193)

The present invention relates to metal casting and more particularly to resin-sand blends from which to provide molds and cores for metal founding and casting.

Castings made of metal and particularly the light metals such as aluminum and alloys of the same, are usually frangible in nature. In the case of solid castings, this calls for exercise of care in handling them. When these castings are provided with cavities, the problem becomes more acute. In particular, disengagement of the solidified castings from the sand cores used in their production can easily, and often does, result in damage to the castings.

The facility with which the mold core can be disengaged from the cavity of a casting is known as its collapsibility. Ideally, in accomplishing this, the mold core should be capable of reverting to a pulverulent form, much the same as the sand from which it was originally shaped, after the cast metal has become solidified, so that it can be more or less poured out of the cavities following gentle tapping or shaking. To state it in another manner, the mold core, and more specifically, the resin used as binders in the same should evidence the characteristics of being resistant to erosion by the metal during casting but capable of being substantially broken down by the sensible heat which remains after the casting has become solidified.

For the most part, the collapsibility of sand cores used in casting light metals such as aluminum etc. and their alloys, utilizing the binder compositions available to date, has been poor, or at least less than acceptable for use in modern permanent mold casting operations which are carried on at relatively low molding temperatures. Mold cores using conventional core oils, urea-formaldehyde and phenolic binders in operations such as this, remain uncollapsed after the castings have cooled to room temperature and perforce the sensible heat of the casting has been spent. As a result, the castings must be subjected to added operations of hand cleaning and/or baking at high temperatures for extended periods of time, or to special vibrating fixtures in order to collapse or disengage the cores from the cavities formed in the castings.

Accordingly, it is a principal object of the present invention to provide sand-resin blends, which when used to form sand molds and sand cores for metal casting can exhibit fast collapsibility even though relatively low temperatures are used in the casting operations.

Another object is to provide phenol-formaldehyde resins which after being used in preparing the preceding sand-resin blend and acting as resin binders for sand molds and cores made from the same can be subjected to casting conditions and remain water-sensitive or capable of being leached out by water.

Other objects will in part be obvious and will in part appear hereinafter.

These and other objects of the invention are attained by utilizing sand-resin blends in sand molds and sand

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cores adapted for metal casting operations, said resin comprising a liquid water-dilutable partial condensate in mol ratio of 1-3 mols of aldehyde per mol of phenol, said partial condensate being the type produced by an alkaline catalyzed condensation reaction carried out at a pH of 8.0-11.0 and thereafter readjusted to a pH of 6.0-8.5 by the addition of boric acid. In describing the partial condensate as "liquid" the meaning intended to be conveyed is that the resin constitutes resin solids in an aqueous medium. The preferred resin solids content will be defined hereinafter.

The following examples are provided in illustration of the invention, where parts are mentioned, parts by weight are intended unless otherwise described.

EXAMPLE I

To a reaction vessel fitted with an agitator, heater and vacuum reflux condenser, add 100 parts of phenol, 210 parts of 37% formalin and a solution of 5.5 parts of sodium hydroxide in 5.5 parts of water. The mixture is allowed to react at a temperature of about 75° C. for three hours, or until about 2% free formaldehyde remains, as determined by the hydroxylamine hydrochloride test.

Add 6.5 parts of boric acid to readjust the pH of the reaction mixture to 8.0 and cool to 20-30° C. to arrest the condensation reaction. Agitation is maintained during cooling. The reaction product is an adjusted water-dilutable liquid partial condensate or liquid resin of phenol and formaldehyde having a viscosity of about 100 centipoises (Ostwald) and a solids content of about 48%-52% (Owens).

EXAMPLES II-VIII

In the manner of Example I, a series of water-dilutable, liquid resins of phenol and aldehyde are prepared using the following constituents and amounts:

Table I (Parts by Weight)

Example	II	III	IV	V	VI	VII	VIII
Phenol.....	100	100	100	100	100	100	100
Aldehyde.....	¹ 177	² 210	² 210	² 210	² 210	² 180	² 210
NaOH.....	6.0	6.0	5.0	4.0	5.0	5.5	6.0
Water.....	6.0	6.0	5.0	4.0	5.0	5.5	6.0
Boric acid.....	7.0	7.0	6.0	4.7	6.0	6.5	6.0

¹ 160 parts of formalin and 17 parts of paraform.

² Formalin.

EXAMPLES IX-XVI

Each of the liquid resins prepared in Examples I-VIII above is blended with a quantity of round-grained reference sand (Ottawa-60) in a laboratory muller for a period of three minutes. The amounts used are in the proportions of 3 parts by weight resin solids per 100 parts of sand. Add to each of the mixtures 0.5%, on the weight of the sand, of a mixture of 7 parts of kerosene to 1 part of oleic acid, as a core release agent, and continue blending for an additional 45 seconds. The sand-resin blends which result are cohesive masses having about .5 p.s.i. green strength.

Fifteen AFS (American Foundry Society) test core specimens from each (total of 120 specimen cores) of the preceding sand-resin blends are made by ramming approximately 113 gram portions into a test mold (dog bone)

using a hand rammer. The specimens are baked in a circulating air oven at 110° C. for periods of 15, 30, 40, 50 and 60 minutes (3 specimens at each temperature).

Each of the specimen cores is placed in a Universal Sand Tester and tensile strength is observed. The results follow:

Table II

Example	Bake time, min./inch				
	15	30	40	50	60
	Tensile strength/p.s.i.				
I and IX	189	187	194	196	196
II and X	180	212	246	290	349
III and XI	215	330	330	350	380
IV and XII	170	200	210	210	210
V and XIII	180	208	208	220	220
VI and XIV	180	215	210	215	220
VII and XV	189	225	225	230	235
VIII and XVI	190	199	210	220	235

The broken pieces of the specimen cores remaining after tensile testing, are placed in equal quantities of water. The period required to dissolve each is observed. The rate at which solubilization takes place is found to be essentially a function of bake or cure time. However, even those cores baked for the longer periods evidence water-sensitivity. In view of the foregoing tensile data and solubility behavior, it can be concluded that added resistance to metal erosion by the molds and cores is attained, the erosion to be anticipated during casting operation, by longer baking periods, without complete loss of water-sensitivity. The ideal bake time can be chosen in view of the melting point of the metal to be cast. Illustration: when aluminum or other relatively low temperature melting metal is to be cast, a bake time on the order of 15 minutes per inch can be used, while those cores baked for 40–50 minutes per inch can be used in casting iron, ferrous metals and other metals having approximately the same melting points. With higher melting alloys such as steel, the molds and cores of the present invention, which have been subjected to bake times of 60 minutes per inch, can be used.

Three additional specimens of each of the same liquid resins (total of 24 specimen cores) are made in the manner preceding with the exception that curing of the specimens is by dielectric heating at 450 milliamperes for a period of 45 seconds per inch. The cores have adequate tensile strength and exhibit water-sensitivity. The fact that the resin binder compositions can be cured by dielectric means to form cores useful in metal founding and thereafter retaining water-sensitivity is distinctive.

EXAMPLE XVII

Three parts by weight on the solids, of the resin binders prepared in Examples I–VIII are blended each with 100 parts of Whitehead "D" sand (Whitehead Bros.—New Jersey) for 3 minutes in a laboratory muller, followed by addition of 0.5% on sand weight of the core release used earlier, and blending continued for 45 seconds. The sand-resin blends are blown into 6 identical "core" shapes (total of 48 cores) and baked for 30 minutes/inch thickness at 110° C. in a circulating air oven. The cores are then placed in shell molds and cast in aluminum to produce valve bodies having wall thicknesses ranging .125–.25 inch. After solidifying and cooling to room temperatures, the castings are soaked in water for a period of 10 minutes and the cores are immediately flushed out when a stream of water under 40 p.s.i. is directed on them. On observation, the cavities of the valves retain none of the sand core material, and the inner surfaces of the cavities are extremely smooth, exhibiting no chips, cracks or damages.

The sand-resin blends of the present invention utilize as a resin composition, a liquid water-dilutable partial

codensate in mol ratio of 1–3 mols of aldehyde per mol of phenol, said condensate being of the type which is produced by an alkaline catalyzed condensation reaction carried out at a pH of 8.0–11.0 and thereafter readjusted to a pH of 6.0–8.5 by the addition of boric acid.

In producing the desired liquid water-dilutable partial condensates, the first step is that of partial condensation or reaction of phenol and aldehyde under alkaline catalytic conditions. The reaction can be carried out at temperatures of 60° C.–100° C. and pressures of 25" Hg (vacuum) to atmospheric. During the condensation reaction, the pH is maintained at 8.0–11.0 and more preferably 8.5 to 10.0. Reaction is continued until 1.0–3.0, more preferably 1.2 to 2.5 mols of aldehyde per mol of phenol on a mol ratio have been reacted.

In order to check for water-dilutability, which is a necessary attribute of the reaction product, a simple test method prescribes adding water at 25° C. to samples taken from the reaction medium until a haze or cloud occurs. The dilutability is expressed as volumes of water required per volume of original resin solution to form the haze or cloud. The reaction is terminated at the desired dilutability between 1 to 1 and 24 to 1 or greater, and preferably between 10 to 1 and 20 to 1.

Arrest of the reaction is had by cooling to 20–30° C. While cooling is being carried on, a quantity of boric acid is added to the reaction mixture and thoroughly dissolved and mixed throughout by use of agitation. The pH is accordingly readjusted to 6.0–8.5 with the further preference of 7.5 to 8.2. This is also the final pH of the liquid resin.

The liquid resin binders preferably have a viscosity range of 50 to 500 centipoise (Ostwald) and a solids content of 40–60% and more preferably 45 to 55% (Owens). To attain this, the reaction mixture, if so required, can be subjected to vacuum concentration or other extraction procedures. Additionally, the liquid resin can be brought to higher solids content for ease in handling followed by addition of water at the source prior to blending. The occasion to use lower resin solids content than that shown as preferred is extremely remote.

The reactants utilized in producing the desired partial condensates are aldehydes and phenols. The aldehydes to be used include formaldehyde in its various forms, such as formalin (35–50%), paraform (91–100%) etc. A portion of the preceding may be replaced with furfuraldehyde. The phenols to be used include phenol, and meta substituted phenols such as the methyl, ethyl, phenyl meta substituted phenols. As indicated, the condensation reaction is of the alkaline catalyzed type. Catalysts can include sodium hydroxide, lithium hydroxide and other soluble bases which form borate salts soluble in phenolic resins of this type. The amount of alkaline catalyst is preferably equivalent to 3.0 to 6.0 parts of NaOH, or sufficient to give reaction conditions of 8.0 to 11.0 pH. The boric acid which is later added to the reaction mixture can be any of the usual forms including ortho-boric acid, meta-boric acid, pyro-boric acid, per-boric acid, benzyl boric acid, ethyl boric acid and other aryl and alkyl substituted boric acids, as well as boric acid complexes as exemplified by boro tartaric acid, boromolybdic acid and the like. The amount of boric acid to be used is sufficient to readjust the pH of the partial condensate to 6.0 to 8.5.

The sands which can be used in producing the resin blended sands of the present invention can be any of those which are usually used in metal founding, including round grained sand, subangular and angular grained sands. Mixing of the sand and resin binder can be carried on in mullers and other mixing apparatus. The preferred amounts of binder to be used ranges in the ratio of between 0.5–10.0 parts per weight determined as resin solids on 100 parts by weight of the sand.

Cores produced from the sand-resin blends of the present invention can be baked at 100° C. to 250° C. as well as by dielectric heating. As indicated, the times and tem-

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peratures for baking depend upon the melting points of the metals to be cast. When high temperature baking is used, shorter baking periods can be enjoyed. It is also possible to shorten the period required for baking or curing by adding caustic material immediately prior to or during curing. Various adducts can also be included in the cores such as cereals including corn and wheat flour to add green strength; mold release agents including oleic acid-kerosene mixtures; thickening agents such as carboxymethyl cellulose etc.

The cores produced from the sand-resin blends of the present invention can be used for metal casting carried out in dried plaster molds, shell molds, green sand molds, dry sand molds, permanent molds, centrifugal casting molds. The sand-resin blends can also be used in making the dry sand molds themselves.

Various metals and alloys can be cast in the molds and around the cores utilizing the sand-resin blends of the present invention. As indicated in the exemplary material above, the baking or curing times for setting the cores and molds will be determined in accordance with the melting points of the metals or alloys involved. These can include the lower melting point metals such as aluminum, magnesium and zinc alloys, ranging up to 760° C.; valve metals, brasses, bronzes and the like up to 1230° C.; grey iron, nodular iron and malleable iron up to 1535° C.; low carbon steels, stainless steels up to 1760° C. and refractory metals and alloys above this. For the higher melting metals it may be advantageous to incorporate a certain amount of other one-stage resins in order to contribute higher tensile strengths to the cores and molds while retaining the collapsibility characteristics of the resin of the present invention. As indicated previously, the invention has peculiar adaptability to casting of metals having the lower melting points.

It will thus be seen that the objects set forth above among those made apparent from the preceding description, are efficiently attained and since certain changes may be made in carrying out the above process without departing from the scope of the invention, it is intended that all matter contained in the above description shall be interpreted as illustrative and not in a limiting sense.

What is claimed is:

1. A process for producing dry sand molds and cores capable of exhibiting fast collapsibility when used in metal casting operations the said process consisting of the steps of (a) shaping molds and cores from a sand-resin mixture, the resin consisting essentially of a water-dilutable

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liquid condensate in mol ratio of 1-3 mols of aldehyde per mol of phenol, said condensate resulting from a condensation reaction carried out at a temperature of 60-100° C. and at a pH of 8.0-11.0 until the reaction mixture has a water dilutability of from 1:1 to 24:1 and thereafter readjusted to a pH of 6.0-8.5 by the addition of a boric acid, then (b) setting the shaped molds and cores by curing the resin to a point wherein it has water-sensitivity.

2. The process according to claim 1 wherein the partial condensate contains in mol ratio 1.2-2.5 mols of formaldehyde per mol of phenol.

3. The process according to claim 1 wherein the partial condensate is readjusted to a pH of 7.5-8.2 by the addition of boric acid.

4. Dry sand molds and cores capable of exhibiting fast collapsibility when used in metal casting operations, said molds and cores consisting essentially of a sand-resin mixture, the resin consisting essentially of a water-dilutable liquid condensate in mol ratio of 1-3 mols of aldehyde per mol of phenol, said condensate resulting from a condensation reaction carried out at a temperature of 60-100° C. and at a pH of 8.0-11.0 until the reaction mixture has a water dilutability of from 1:1 to 24:1 and thereafter readjusted to a pH of 6.0-8.5 by the addition of a boric acid, the said resin having been cured during setting of said molds and cores to a point wherein it has water sensitivity.

5. The dry sand molds and cores according to claim 4 wherein the partial condensate contains in mol ratio 1.2-2.5 mols of aldehyde per mol of phenol.

6. The dry sand molds and cores according to claim 4 wherein the partial condensate in mol ratio 7.5-8.2 by the addition of boric acid.

References Cited in the file of this patent

UNITED STATES PATENTS

2,706,188	Fitke et al. -----	Apr. 12, 1955
2,797,457	Kramer -----	July 2, 1957
2,856,381	McNaughtan et al. -----	Oct. 14, 1958

FOREIGN PATENTS

715,293	Great Britain -----	Sept. 8, 1954
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OTHER REFERENCES

The Foundry, pages 96 and 206, August 1950.
 Foundry Practice, page 7, April 1948.
 Phenoplasts, T. S. Carswell, pages 11-12, 1947.