United States Patent Office 2,706,163
Patented Apr. 12, 1955

2,706,163

COATED SAND AND METHOD OF PRODUCING THE SAME

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No Drawing. Application June 5, 1953, Serial No. 359,950

5 Claims. (Cl. 117—72)

This invention relates to improvements in the production of sand precoated with resin and particularly adapted for use in the "shell molding" process.

More particularly, the present invention relates to improvements in the method of producing storage-stable, free-flowing sand particles whereby each sand grain is provided with a solid, nontacky enveloping coating of potentially thermosetting phenolic resin and an outermost coating of solid, nontacky, unctuous material, and to the novel properties, utility and advantages of the resulting product.

The "shell molding" process for the production of sand mold sections for the casting of metals as known in the prior art has in general comprised the employement of an essentially dry mixture of sand and powdered resin and when required powdered resin curing and accelerating agents, and the depositing of such mixture against the face of a heated metal pattern coated with a lubricating or release agent such as a silicone resin. This is generally accomplished by placing the aforesaid dry mixture in the bottom of a pivotally supported or other container with the top closed by the metallic pattern. After the pattern is preheated to about 400–500° F., the container is inverted so that the sand-resin mixture is thrown against it, and in less than a minute the resin melts and fuses and forms a unitary crust of from about ⅛ to about ½ inch in thickness. Excess sand-resin mixture, which has not been reached by heat in an amount to fuse the resin, is removed for subsequent use, and the preliminary shell or crust on the pattern is subjected to further heat, as in an oven, to cure the resin to the thermoset or infusible condition. It is then separated from the pattern in the form of a rigid shell mold section ready for use for the casting of metals.

As distinguished from the employment of dry sand-resin mixtures in the aforesaid process, the copending applications of Fitko and Horn, Serial Nos. 297,396 filed July 5, 1952, and 346,534 filed April 2, 1953, teach the production of storage-stable, free-flowing sand grains, each provided with a solid, nontacky coating of potentially thermosetting phenolic resin for use in the aforesaid shell molding process in lieu of the dry sand-resin mixture. This eliminates dust and explosion hazards of a powdered mix, avoids separation and stratification of the components, permits employment of conventional foundry sand handling equipment, permits the production of shell molds of more uniform character and of improved physical properties, and saving in the amount of resin required.

It is one object of the present invention to eliminate the necessity for coating the metal pattern, in the aforesaid process of forming shell molds, with lubricants or release agents. This is accomplished in accordance with the present invention by combining with or building into the resin coated sand described and claimed in the aforesaid copending applications, an unctuous material which is adapted to act as a lubricant or release agent when the coated sand is applied to a metal pattern in the aforementioned process for producing the shell molds.

The combination of the unctuous material with the particles of resin coated sand results in other advantages, such as improved strength of the shell molds and better density and thus greater resistance to hot metal penetration and higher fidelity of casting surfaces.

Further advantages in the forming of the shell molds are reduction in tendency of the preliminary shell or crust to fall off the pattern prematurely when inverting the dump box to remove excess sand, or "peelback" when the

pattern and shell are lifted and separated from the dump box. "Peelback" may be defined as splitting of the preliminary shell into two parts, namely, a thin crust which remains on the pattern and a hot plastic layer which drops back into the dump box and contaminates the remaining coated sand, caused, at least in part, by the sticking of the hot plastic sand to the rim of the dump box above and surrounding the metal pattern.

Further advantages arising out of the use of the unctuous additive in the process of coating the sand with resin are the economies and facility of the mixing and coating process, such as great reduction in power consumption for a given quantity of sand being handled in a mixer or ability to handle much larger quantities of sand; for example, two and one-half times as much as without said additive, for the same power consumption, all with pronounced saving in wear and breakdown of mixing equipment.

The particles of resin coated sand with their overcoat of the unctuous material are further characterized by their soft, silky, and enhanced free-flowing storage-stable character.

The processes of the aforementioned Fitko and Horn copending applications for coating sand with resin comprise in general the placing of foundry sand into an intensive mixing vessel, together with from about 2 to 4% by weight of the sand of acid-catalyzed, neutralized, fusible phenol-formaldehyde resin, i. e. Novolak. These are mixed together to uniformly distribute the resin over the individual sand grains, with the aid of heat adequate to maintain the resin in liquid condition. While the resin is still in liquid condition and while continuing mixing, there is added about 8 to 20% of hexamethylenetetramine by weight of the resin and the two permitted to partially react until the melting point of the resin on the sand is raised about 10 to 25° C., and in any event above about 80° C., to an upper limit of about 102° C. when employing resins initially introduced in normally liquid form, or to an upper limit of about 115° C. for resins which were introduced in normally solid form. At this point the mix is cooled, or permitted to cool, below the desired new melting point of the modified resin, and to arrest further reaction, while continuing mixing and cooling to reduce the mix to discrete particle form.

The recovered product is a dustless, free-flowing, nontacky material consisting of particles of sand separated from adjacent particles and wherein each sand particle is coated with a film of potentially thermosetting resin nontacky at normal room temperature, capable of being converted into a coalesced mass by the application of heat sufficient to melt the resin coating and with substantially no pressure capable, by coalescence of the resin films, to form a continuous resin matrix wherein the sand particles are substantially uniformly dispersed to form a rigid structure, said rigid structure being capable of being further heat hardened by cure of the resin to the infusible or thermoset condition.

The normally liquid resin referred to may be one formed of from about 0.5 to about .725 mol of formaldehyde per mol of phenol having a solids content of from about 70% to about 80%. When mixed and heated with the sand at a temperature of about 100° C. for five to ten minutes, the volatiles are removed and the liquid resin, in the absence of any added reactant, is converted to a potential solid of 60–65° C. melting range. Addition of the hexamethylenetetramine during this period causes reaction, and reaction is terminated by cooling when the modified melting point of the partially reacted resin on the sand has advanced to a melting or softening range of 80–102° C.

The normally solid resin referred to may be formed of from about .75 to .9 mol of formaldehyde per mol of phenol. This can be employed in molten form or added to the sand in the form of tarred briquets, flakes, chips or grains. Employment of the solid resin permits use of higher melt point of the resin on the coated sand, so that on addition of hexamethylenetetramine, partial reaction therewith and advancement to a melt point as high as 115° C., before cooling and arrestment of further reaction, may be permitted.

Mixing, heating, and controlled limited reaction may

be conducted in suitable, known mixing devices, such as a Werner-Pfleiderer mixer, a Beardsley-Piper mixer, or a Simpson muller. The liquid resin, or the solid resin in either solid or preliquefied condition, is added to the sand to be coated in the vessel, with the aid of heat to melt or maintain the resin in liquid condition for coating of the sand grains, and for the purpose of permitting partial reaction with the added hexamethylenetetramine. Depending on the type of mixing apparatus employed, heating may be accomplished by means of heated air directed through the mixing vessel, or by employing a vessel having a steam jacket, or merely employing an adequately preheated sand. Termination of heating at the desired point may be accomplished by addition of cooling water or by loss of heat of the originally preheated sand, as more particularly described and claimed in the copending application of Murphy and Albanese Serial No. 346,508, filed April 2, 1953.

Control of the melting point or range of the resin on the sand and limitation thereof to the indicated degree limits the extent of reaction between the Novolak resin and the hexamethylenetetramine to a condition where there is some reaction between the two, as indicated by the advance in melting point, but yet where some lies dormant or "locked in," so that the resin coating may be said to be in a potentially thermosetting condition, since all necessary hexamethylenetetramine for such purpose on further heating is present. Arresting the reaction at this point leaves the resin in a condition of desirably good flow requisite for obtaining good bonding without pressure and good tensile of bonded sand particles, when they are employed in the production of shell molds by the means previously described.

Sands employed may be those such as washed and dried AFS silica sand with a 100 fineness number, Wedron 50 sand, and the like foundry sands.

In accordance with the present invention, and for the attaining of the objects and advantages previously described, an unctuous additive is further introduced to the mixing vessel and heated and mixed with the sand, resin and hexamethylenetetramine, prior to the cooling stage, so that the unctuous material may be melted and uniformly distributed in the mixer. The unctuous material should be miscible with or dispersible in the molten resin, but only of limited solubility therein and have a melting point at least substantially that of, and preferably higher than that of the resin, so that it precipitates out of the hot resin on cooling, forming a thin layer on the resin surface and a uniform coating, as distinguished from becoming entrapped within the resin or at least producing droplets on the resin surface, as might be the case when employing soluble materials and those having a melting point lower than that of the resin. The use of unctuous materials of hard character and having melting points higher than that of the resin is further preferred so as to increase the tensile strength of the end product i. e. shell molds, rather than weaken them, as would be the case if the melting point of the unctuous material were relatively low. Thus for the practice of the present invention the unctuous additives should in general have a melting point above 80° C., and preferably above about 85° C. (185° F.)

The suitable unctuous additives are waxes or wax-like materials which, as indicated, are hard, have high melting points, and separate out and precipitate onto the resin surface on cooling. They may be employed in amounts as low as about 0.5% by weight of the resin, as in the case of hard, high melting point microcrystalline waxes, such as oxidized microcrystalline wax, Estawax 25, which is hard and has a melting point of about 99° C., and as low as about 2–3% with others, as for example Acrawax C, a hard synthetic wax having a melting point of 140–143° C., described in U. S. Patent 2,429,664, as a substituted polyamide of stearic acid. The employment of such hard waxes additionally improves the tensile strength of products formed from the coated sand. Although a microcrystalline wax of about 82° C. melting point, such as Warco 180, precipitated onto the surface of a resin having substantially the same melting point and gave the desirable unctuous character, it did not improve tensile strength. Paraffin waxes with their much lower melting points are of little benefit and form droplets locked within the solidified resin.

Other suitable unctuous materials are the waxy medium molecular weight polyethylenes melting above about 85° C., such as Alcowax 7 which melts at 102–106° C., methylene bis-stearamide melting at about 132° C. (Armowax), and calcium, lithium and zinc stearate.

These unctuous additives may be added in either solid, powdered, molten or solution form, and at any time prior to or during the heating and mixing of the other materials in the mixing vessel and before cooling of the molten resin, and separately or with the introduction of the resin or hexamethylenetetramine.

The following examples are for the purpose of illustrating, but not limiting, the present invention:

4540 grams of washed Wedron 50M sand was heated to 285–290° C. and placed in an eighteen-inch open Simpson laboratory muller. To this was added 125 grams of normally liquid Novolak resin, of the kind previously described, and the mixture mulled for fifty seconds. Then 12 grams of powdered hexamethylenetetramine was added and the mulling continued. After about four minutes the resin coated sand had cooled, by transfer of heat through the metal mixer and to the atmosphere, to below its now modified melt point, and the doughy mass began to break up. Further mixing for five minutes broke up the clumps of resin coated sand to a free-flowing material which was then screened and ready for use. The melting point of the resin on the sand was 88° C. Standard tensile briquets prepared therefrom according to the American Foundryman's Society specification exhibited an average tensile strength of 305 pounds per square inch.

The same procedure was followed as in the foregoing example, except that Acrawax C as an unctuous material was added in varying amounts and with either the resin or the hexamethylene, with the following results as compared to the control:

Percent Acrawax C by weight of resin	Time of Addition	Melting Point, ° C.	Tensile Strength, p. s. i.
0		88	305
2	with hexa	95	512
4	do	99	490
8	do	101	405
2	with resin	92	516
4	do	96	552

The product resulting from the use of the unctuous additives was of an enhanced free-flowing nature and of silky texture, with the resin coating on the sand enveloped by a thin layer of unctuous material. The muller ran extremely quiet and smooth and the surfaces of the vessel remained clean. The test briquets were of about 13% increased density over the control. Shell molds prepared from the resin coated sand including the unctuous material envelope, employing a clean pattern surface, exhibited substantially complete absence of "fall off" and only minor edge "peelback," and did not require any other lubricant or parting agent. The indicated improvements in tensile strength were a marked advantage.

The following table illustrates the improvements of the melting point on the resin and/or increased tensile strength obtained from a variety of waxes or waxy materials, all of which precipitated out on the surface of the resin coating on sand to provide a desirable unctuous film, as compared to a control prepared in a manner similar to that of the preceding example:

Additive	Percent by Weight of Resin	Melting Point of Coating on Sand, ° C.	Tensile Strength, p. s. i.
Control	None	88	268
Acrowax C	2	91	390
Armowax	2	89	365
Calcium stearate	2	90	385
Lithium stearate	2	88	390
Zinc stearate	2	89	360
Warco 180	2	92	240
	0.5	88	270
Estawax 25	2	88	305
	1	84	310
Alcowax #7	0.5	88	427
	2	84	342
	0.5	88	382

It is claimed:

1. A dustless, free-flowing, nontacky molding sand consisting of sand particles wherein each particle of sand

is separated from adjacent particles and wherein each sand particle is coated with and completely enveloped by a blended dual-layer hard film nontacky at normal room temperature composed of an inner film layer of potentially thermosetting resin and an outer film layer of heat liquefiable waxy material in the proportions of from about 2 to 4% of resin by weight of the sand and from about 0.5 to 8% of waxy material by weight of the resin, said waxy material having a melting point at least that of the resin and substantially insoluble therein in solid condition.

2. The method of coating sand grains with individual coatings of solid, nontacky, potentially thermosetting resin enveloped by a film of hard nontacky waxy material, which comprises mixing acid-catalyzed fusible phenol-aldehyde resin, normally hard and solid heat liquefiable waxy material, and hexamethylenetetramine in an amount adequate to ultimately convert the resin to a thermosetting condition, with sand at a temperature above the melting points of the resin and waxy material to uniformly distribute them and to substantially uniformly coat the sand grains with the molten materials in the proportions of from about 2 to 4% of resin by weight of the sand and from about 0.5 to 8% of waxy material by weight of the resin, cooling the mixture after partial resin conversion reaction to below its resulting modified melting point to arrest said conversion reaction and to solidify the resulting potentially infusible resin and to further precipitate and solidify thereover a film of said waxy material, said waxy material being miscible with the resin in their jointly liquid condition and substantially insoluble therein in solidified condition and having a melting point at least substantially equal to that of the solidified resin coating on the sand, and containing the mixing during cooling to solidification to separate aggregates in the mix and recovering a mass of unctuous free-flowing coated sand grains composed of particles of sand individually coated with a solid nontacky layer of potentially thermosetting resin and an outermost enveloping solid nontacky film of said waxy material.

3. Free-flowing, storage-stable particles of sand individually coated with from about 2 to 4% by weight of

a solid, nontacky layer of potentially thermosetting resin, said resin layer carrying an outermost enveloping film of solid nontacky heat liquefiable waxy material having a melting point at least substantially that of the resin coating on the sand and substantially insoluble therein in solid condition and in the proportion of from about 0.5 to 8% by weight of the resin.

4. Discrete, free-flowing, storage-stable particles of molding sand individually coated with from about 2 to 4% by weight of a solid nontacky layer of potentially thermosetting resin composed of normally thermoplastic phenol-formaldehyde resin including and partially reacted with hexamethylenetetramine, said resin layer carrying an outermost enveloping film of solid nontacky heat liquefiable waxy material having a melting point at least substantially that of the resin coating on the sand and substantially insoluble therein in solid condition and in the proportion of from about 0.5 to 8% by weight of the resin.

5. Free-flowing, storage-stable particles of molding sand adapted for the production of shell molds of increased density and tensile strength, composed of particles of sand individually coated with from about 2 to 4% by weight of a solid nontacky layer of potentially thermosetting resin and an all-enveloping film of solid, nontacky, hard, heat liquefiable waxy material adapted to act as a pattern lubricant in the proportion of from about 0.5 to 8% by weight of the resin, said waxy material having a melting point at least substantially that of the resin coating on the sand and substantially insoluble therein in solid condition.

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