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# SHELL MOLDS AND CORES FROM PRECOATED FLUID COKE

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The present invention relates to improved shell molds and cores, and to compositions for forming shell molds and cores. It more particularly pertains to an improved shell mold composition comprising fluid coke and a minor proportion of a resin binder.

This application is a continuation-in-part of S. N. 539,778 "Carbonaceous Molding Material for Foundry Operations," filed October 11, 1955 by the present inventors.

In brief compass this invention proposes a shell molding composition comprising a major proportion of fluid coke, either raw, calcined or calcined and desulfurized, and a thermal setting resin binder. The resin binder is distended on the particles of fluid coke, i. e., the fluid coke is precoated with the resin binder.

The hydrocarbon oil fluid coking process has recently been introduced into petroleum refinery operations. In this fluid coking process, an oil, usually a low value heavy residual oil, is converted by pyrolysis to relatively lighter hydrocarbons and coke by contact with finely divided heat carrying solid particles maintained at a temperature in the range of 850° to 1500° F. or above. The heat carrying solids are preferably maintained as a fluid bed in a coking zone, but the process can be carried out in a transfer line. The coke produced by the pyrolysis deposits on the fluidized solids, layer by layer, and becomes a part thereof. Although some of the coke produced by the cracking may be consumed by burning to supply heat in the coking process, a substantial amount is removed as by-product. The heat carrying solids normally used are coke particles produced by the process such that the by-product coke is of uniform composition. The by-product fluid coke produced has a high percentage of carbon with an ash and sulfur content characteristic of the oil feed stock.

The particle size of the heat carrying solid used in the coking process is in the range of about 18 to 400 U. S. sieve number, with the median particle size normally being in the range of 45 to 70. The by-product coke is of about the same size. This unique by-product coke is characterized by its spherical or ovoid shape, laminar structure, high density and hardness, and differs substantially from the cokes produced by the pyrolysis of hydrocarbonaceous solids and oils by other processes. The term "fluid coke" is intended to include the solid product of the fluid coking process, i. e., the by-product coke or "raw" fluid coke, besides the treated forms of the raw fluid coke, described below.

It is much preferred to pretreat the raw fluid coke received from the coking process, by calcination and/or desulfurization to decrease its volatile matter and sulfur content and to increase its density. The product so obtanied by this pretreatment is hereinafter referred to as calcined fluid coke. Although desulfurization treatment of raw fluid coke normally results in calcination of the coke, it is not necessarily always true. The term "calcined fluid coke" herein used, includes fluid coke that has only been desulfurized. Calcined fluid gives many superior and unexpected results over raw fluid coke.

Calcination of the raw fluid coke to primarily increase its density and decrease its volatile matter content may be carried out by any conventional method. Generally, calcination of fluid coke simply involves heat soaking at

relatively high temperatures, e. g., 1800° F. or above, for a suitable period of time. This is preferably done separate from the coking process, but may be carried out within the process, as by segmenting the burner used to heat the circulating fluid coke to form a special high temperature zone from which the by-product coke can be withdrawn. The calcination or heat soaking may be carried out while the fluid coke is in the form of a fixed, gravitating or fluid bed. A preferred method of calcination is to quickly heat the raw fluid coke up to about 2400° to 2800° F. by direct contact with high temperature flue gases or products of combustion, and then to quickly separate the heated coke from the gases. The coke so heated is then maintained as a gravitating bed in a refractory lined soaking chamber for about one hour to complete the calcination. In this preferred manner of operating, volatile sulfur compounds, relatively undiluted with flue gases, can be recovered from the soaking zone.

It will be apparent to those skilled in the art that raw fluid coke can be calcined by repeated use in the casting process, and the term "calcination" is intended to include this. Thus, a small amount, say 5%, raw fluid coke can continuously be added to the reservoir of material used to form molds and/or cores in a foundry, and by repeated use become suitably calcined.

Desulfurization of raw fluid coke or of fluid coke that has been calcined can be accomplished in several ways. One preferred method is to oxidize the coke by fluidizing it with an oxygen containing gas at a temperature in the range of 600° to 1500° F. for a time sufficient to consume over 3 weight percent of the fluid coke. An especially preferred method of desulfurization comprises this oxidation treatment followed by hydrogenation with a free hydrogen containing gas at temperatures above 1100° F. In some cases the fluid coke may be desulfurized without preliminary heat soaking, by contact with a desulfurizing gas such as hydrogen, ammonia, sulfur dioxide, etc. When using hydrogen it is preferred to maintain the temperature above 1100° F.; when using sulfur dioxide, the temperature is preferably maintained above 1800° F. Also, pressures of about 35 to 1000 p. s. i. or above are useful during desulfurization.

Instead of treatment with a desulfurizing gas, the coke can be desulfurized simply by a high temperature thermal treatment. Thus, at temperatures of about 2400°–2800° F., the sulfur compounds in coke can be broken down and driven off. At the lower temperature, several hours of heat soaking may be required to remove the sulfur.

In some uses it may be preferred, besides calcining the coke, to further pretreat it as by treatment with a solvent or by impregnating it with a suitable material such as water glass or finely divided graphite to decrease its porosity.

Fluid coke as removed from the fluid coking process, when coking the customary residual oil feed stocks, normally will have a sulfur content of about 7 weight percent or above. It is preferred to reduce the sulfur content if necessary, by the above treatments, to below about 7 weight percent to prepare it for use in foundry operations because higher amounts of sulfur may produce intolerable amounts of noxious fumes. Raw fluid coke can, however, itself be used in casting operations as hereinafter described.

To illustrate the change in properties that occurs during different treatments of raw fluid coke, Table I is presented. The examples given for each type of coke are based on raw fluid coke having an original median particle size of about 235 microns, obtained by the fluid coking of a Hawkins residuum having a gravity of 4.3° API, a Conradson carbon of 26 wt. percent, an initial boiling point of 882° F. (atmos. pressure equivalent), and a 10% point of 1010° F. The coking was at a temperature of about 1000° F.

The calcined fluid coke example is based on treating raw fluid coke as a gravitating fluid bed in an elongated vertical calcining chamber, at a temperature of about 2100° F. for a time up to about 15 hours.

The desulfurized fluid coke example was obtained by treating raw fluid coke as a gravitating moving bed in an externally heated elongated vertical silicon carbide brick-lined calcining tower. The coke was heated to a temperature up to about 2400° F. for a time of about 24 hours, in the presence of a small amount of nitrogen stripping gas.

TABLE I

| | Examples | | |
|---|---|---|---|
| | Raw fluid coke | Calcined fluid coke | Desulfurized fluid coke |
| Size, A. F. S. No | 52 | 68 | 75 |
| True density, grms./cc | 1.48 | 1.95 | 1.86 |
| Bulk density, lbs./gal | 7.8 | 9.1 | 9.25 |
| Moisture, weight percent | 0.5 | Nil | Nil |
| Sulfur, weight percent | 6.7 | 5.9 | 2.0 |
| Ash, weight percent | 0.6 | 0.8 | 0.3 |
| Carbon, weight percent | 88.3 | ---------- | 97.7 |
| Hydrogen, weight percent | 1.8 | ---------- | Nil |
| Volatile matter, weight percent | 5.6 | 0.2 | Nil |

Generally speaking, calcination of fluid coke normally having a sulfur content of 1–12 weight percent, will reduce its volatile matter content below about 1 weight percent and sulfur content by 5–20%, and increase its true density above 1.7 grms./cc. Desulfurization usually will reduce sulfur content to below 3 weight percent. It is preferred to use fluid coke having characteristics falling in these ranges, as superior results are obtained even over raw fluid coke.

It has now been found that fluid coke precoated with a thermal setting resin binder forms superior shell molds for casting ferrous and non-ferrous metals and alloys thereof. The term "shell mold" as here used includes shell molds, mold liners, shell cores and similar molding forms, generally having a relatively thin wall thickness.

It has been known in the art to precoat sand used in forming shell molds with a resin binder. The resin binder comprises a thermal setting material such as phenol-formaldehydes, urea-formaldehydes, condensates of di-basic acids, and polyhydric alcohols, e. g., of maleic anhydride and pentaerythritol, and similar resins known to the art.

The resin binder may be coated on the fluid coke by known methods. Generally the binder will comprise less than 15 weight percent of the mixture.

In the hot coating or mulling method, the coke is mixed with a liquid resin which may include an accelerator. The mixture is heated, as by using heated air, to cause the resin to coat the coke particles.

In the cold coating method, the coke is coated with a resin using a volatile solvent. More particularly, a powder resin can be mulled with the coke, followed by mixing with an alcohol (e. g., ethyl) solvent and water. The solvent eventually evaporates, leaving the resin deposited on the coke.

Additives can be added to the molding composition before, during, or after coating the particles. For example, sand, mold release agents such as waxes or stearate base materials, or other additives or modifiers to improve green strength, volatility, flowability, etc., such as kerosene, iron oxide, clay, etc. can be added.

When fluid coke is used to form shell molds and cores, shorter investment times can be obtained because of the better heat conductivity of the fluid coke, compared to sand. Lighter shells are obtained. Because of the higher heat conductivity of these shells, better castings are obtained. The shells have better dimensional accuracy because of the lesser thermal expansion of the fluid coke.

The castings from the shells have a smoother surface finish and are less troubled by veining because the shells are formed predominantly of carbonaceous materials. One method of forming a shell mold is to drop or blow the resin coated fluid coke into or onto a heated pattern having a temperature of about 350–750° F. The plastic partially thermal sets and builds up a coherent fluid coke shell next to the pattern. The thickness of the shell is related to the pattern temperature, dwell time on the pattern, and the type mixture. It may vary in thickness from about $\frac{1}{16}$ to one inch or more. The loose fluid coke mixture is then dropped away from the shell, and the shell, still on the pattern, is further cured by heating. The shell is then stripped from the mold. A mold release agent, or parting agent, may of course be used to facilitate the stripping of the shell. Silicone parting solutions are customarily used. The same general procedure can be used for cores. In some cases, the core may be made solid without a central cavity.

### *Example 1*

The fluid coke used was the desulfurized coke identified in Table I. The fluid coke was coated with shell molding resin by the cold coating method for comparison to silica sand coated in the same manner. The resin used was a phenol-formaldehyde type resin, identified as "Durez Resin No. 17786." Table II gives information on the compounding of the resin coated sand and fluid coke. Table III, in columns 1 and 2, gives the sieve analysis of the solids.

TABLE II

| Mix No | 1 | 2 |
|---|---|---|
| Fluid coke (through $\frac{1}{16}''$ mesh), lbs. (See col. 3, Table I.) | [1] 115.5 | -------- |
| Juniata bank sand (A. F. S. No. 96), lbs | -------- | [1] 150 |
| Resin, lbs | 6.0 | 6.0 |
| Methyl alcohol, cc | 900 | 750 |
| Water, cc | 200 | 200 |
| Mixing equipment—Beardsley-Piper Speedmuller. | | |
| Mixing time—40 sec. dry, 3½ min. wet and until dry and free-flowing. | | |
| Shell mold forming technique: | | |
| Equipment—Beardsley-Piper automatic shell former. | | |
| Pattern temp.—400–450° F. | | |
| Oven equipment—Burdett gas burners (no hood). | | |
| Curing temp.—Approx. 1000–1200° F. | | |
| Bonding equipment—Shell Process Inc. bonding fixture. | | |
| Pattern release agent—Dow-Corning XF-496 fluid (silicone). | | |
| Average investment time, seconds | 13 | 15 |
| Average curing time, seconds | 25 | 30 |
| Average shell thickness, inches | $\frac{6}{16}$ | $\frac{5}{16}$ |

[1] Approx. equal volumes.

TABLE III

| Sieve No. | Percent retained on— | | |
|---|---|---|---|
| | 1 | 2 | 3 |
| | Juniata bank sand | Fluid coke through $\frac{1}{16}''$ mesh | Fluid coke reclaimed by heat of iron in shell molds |
| 6 | -------- | -------- | -------- |
| 12 | -------- | -------- | -------- |
| 20 | -------- | 0.3 | 0.3 |
| 30 | 0.1 | 0.4 | 0.7 |
| 40 | 0.3 | 2.7 | 3.1 |
| 50 | 2.2 | 13.3 | 12.8 |
| 70 | 11.9 | 25.9 | 23.5 |
| 100 | 32.8 | 27.6 | 29.1 |
| 140 | 35.4 | 19.4 | 20.5 |
| 200 | 15.3 | 7.3 | 6.5 |
| 270 | 0.3 | 2.3 | 1.7 |
| PAN | 1.7 | 0.8 | 0.4 |
| | 100.0 | 100.0 | 98.6 |
| A. F. S. fineness No | 96 | 75 | 73 |

Calcined fluid coke and the powdered resin were charged into the muller and mixed 40 seconds dry, then the alcohol and water (mixed) were added and mixing continued for about 3½ minutes, by which time the solvent had evaporated and the resin coated particles were again dry and free flowing. The material was then passed through a ⅛-inch sieve to break up any lumps and to assure more complete evaporation of the solvent.

Shell molds were made consecutively with these sand and fluid coke mixtures on the same pattern. The shell former used operated on the dump box principle. From these tests it was determined that the investment time and cure time were less for the resin coated calcined fluid coke molds. Because cure time is usually a limiting factor in the rate of shell mold production, an increase, in this case, of 20% in production due to the higher heat conductivity of the calcined fluid coke is a definite advantage.

The resin coated calcined fluid coke molds were more easily stripped from the pattern and a much less frequent application of silicone release agent to the pattern was required. The fluid coke shell mold could be reseated on the cold pattern, whereas the sand shell mold had shrunk sufficiently to prevent it being replaced on the pattern. The fluid coke shell molds, therefore, are more true to pattern dimensions than are sand shell molds.

### *Example 2*

In another comparative test, resin coated fluid coke and resin coated sand compositions were made up to prepare shell molds for casting generator rotors. Table IV shows the composition and the method of making shells. The coating process was carried out in the same manner and with the same equipment as used in Example 1. The shells were about 9/16" thick. Because of the lighter bulk density of the fluid coke, a slightly larger amount of resin was used in preparing the resin-coated fluid coke mixture, i. e., the bulk density of the fluid coke results in more particles per weight, which necessitates a larger resin content on a weight basis.

TABLE IV

| Mix No. | 1 | 2 |
|---|---|---|
| Fluid coke (through 1/16" mesh), lbs. (See col. 3, Table I.) | 77 | |
| Juniata bank sand (A. F. S. No. 96), lbs | | 150 |
| Resin, lbs | 5 | 6 |
| Methyl alcohol, cc | 550 | 750 |
| Water, cc | 133 | 200 |

Mixing equipment—Beardsley-Piper Speedmuller.
Mixing time—30 sec. dry, 3 min. 20 sec. wet until dry and free-flowing.
Shell mold forming technique:
  Equipment—Hand-operated dump box.
  Pattern temp.—450° F.
  Oven equipment—Enclosed gas burner radiant heat oven.
  Curing temp.—Approx. 1200° F.
  Pattern release agent—Dow-Corning XF-496 fluid (Silicone).
  Bonding equipment—Shell Process Inc. bonding fixture.

Gray iron, melted in an electric furnace, but having the same composition essentially as cupola iron, was poured into test molds at approximately 2600° F.

The castings made of the fluid coke shell mold were somewhat smoother and showed much less penetration around the sprue area than did the castings made in the resin coated sand shell molds. The Brinell hardness for each type of shell mold casting was the same. It appeared, therefore, that no chilling and/or significant sulfur pick up was obtained from the calcined fluid coke shell molds.

It was noted that the heat of the metal burned out the resin in some areas of the fluid coke shell mold, which were well exposed to air, so that the fluid coke dropped away in its original granular form. This was not detrimental to the casting because the metal had solidified before this happened. This behavior did not occur in the case of the sand shell mold, and is attributed to the higher heat transfer characteristics of the calcined fluid coke. A sample of this "burned" calcined fluid coke was recovered and used for rescreen analysis given in Table III, column 3. A comparison of the screen analysis indicates that there was no appreciable change in particle size due to the heat of the metal. It further indicates that some fines may have been burned out and that no appreciable ash was formed. This indicates that the calcined fluid coke can be recycled in molding operations without detrimental effect.

### *Example 3*

In this example, resin coated raw fluid coke was used to prepare shell cores. The fluid coke was obtained by the coking of heavy Elk Basin vacuum bottoms having a Conradson carbon of about 30 weight percent, sulfur of about 4.1 weight percent, I. B. P. of 925–950° F., and an A. P. I. gravity of 0–2°. The coking was conducted at about 960–980° F. at a conversion in the range of 34–36% coke make, based upon fresh feed.

The raw fluid coke had the following typical inspections:

| | |
|---|---|
| Carbon, weight percent | 89.1 |
| Sulfur, weight percent | 6.1 |
| Ash, at 1,742° F., weight percent | 0.11 |
| Volatile matter, at 1,100° F., weight percent | 0.44 |
| Moisture, weight percent | 0.24 |
| Real density | 1.45 |

This raw fluid coke was screened through a 1/16" mesh sieve prior to preparing the resin coated composition.

This raw fluid coke was compared to sand in casting cylindrical gray iron castings weighing approximately two pounds after removal of gates.

Table V lists the core mixtures used to produce the resin coated materials, and the method of making the compositions. The resin used was the resin used in the previous examples. Note that mixtures #1 and #3 have an equal resin content on a volume basis because raw fluid coke weighs approximately 65% the weight of an equal volume of sand.

TABLE V

| Mix No. | 1 | 2 | 3 |
|---|---|---|---|
| Heaton sand (A. F. S. No. 70), lbs. | 10 | | |
| Raw fluid coke (through 1/16" mesh), lbs. | | 6.5 | 6.5. |
| Resin, weight percent* | 4.5 | 4.5 | 6.92. |
| Denatured ethyl alcohol, weight percent.* | 1.33 | 1.33 | 2.05. |
| Water, weight percent* | 0.275 | 0.275 | 0.52. |
| Mixing equipment—Simpson laboratory mixer. | | | |
| Mixing time—1 min. dry, wet | Until dry | 4 min | 7 min. |

*As weight percent in sand or coke.

Note No. 1.—Heaton Sand was screened through No. 30 U. S. mesh before mixing.

Note No. 2.—Mix No. 1, after discharge from mixer, was passed once through No. 30 mesh sieve. Mix No. 2 was passed twice through No. 40 mesh sieve. Mix No. 3 was passed twice through No. 40 mesh sieve.

In producing the shell cores, the core box was heated to equilibrium temperature in a laboratory oven set at 450–475° F. In each case resin coated material was poured into the hot core box, and after suitable dwell time the excess material was vibrated from the inverted box. The core box with the invested shell core inside, was returned to the oven for 20–40 seconds to complete curing of the resin binder. The core box was then parted and the shell removed. The scratch hardness of the cores from mixtures #1 and #3 was approximately 100, while cores from mixture #2 had a hardness of approximately 90.

The shell cores were set in green sand molds and were poured with gray iron melted in a production cupola. On shaking out these castings, it was noted that the raw fluid coke shell cores, bonded with 4.5 weight percent resin, collapsed quickly and the castings were free of adhering core material.

Castings produced from each shell core were cross-sectioned for examination of the cored areas. The surface finish of the cored area of the casting produced with the shell cores from mixture #2 was somewhat smoother than the casting produced with the sand shell cores, both being free of any veinings.

These examples show the superiority of the fluid coke shell molds made by precoating fluid coke with a resin. The fluid coke shell molds are more true to pattern dimensions than similar sand shell molds, and impart smoother surface finish to the castings.

Having described this invention, what is sought to be protected by Letters Patent is succinctly set forth in the following claims.

What is claimed is:

1. A shell molding composition consisting essentially of a major proportion of fluid coke and a thermal setting resin binder, said resin binder being distended on the particles of fluid coke, said fluid coke having been produced by contacting a heavy petroleum oil coking charge stock at a coking temperature with a body of fluidized coke particles in a reaction zone wherein the oil is converted to product vapors and carbonaceous solids are continuously deposited on the coke particles, removing product vapors from the coking zone, heating a portion of the coke from the coking zone in a heating zone to increase the temperature of said fluidized particles, returning a portion of the heated coke particles from the heating zone to the coking zone and withdrawing coke product particles.

2. The composition of claim 1 wherein said binder comprises greater than 0% and less than 15% of said composition.

3. The composition of claim 1 wherein said binder is distended on said fluid coke by dry-mulling the binder with the fluid coke, adding a solvent, continuing the mulling, and then drying.

4. The composition of claim 1 wherein said fluid coke consists of calcined fluid coke having a volatile matter content below 1 weight percent, a sulfur content below 3 weight percent, and a true density above 1.7 grms./cc.

5. A method of making a shell mold, which comprises forming a loose mixture of a major proportion of fluid coke and a thermal setting resin binder distended on such fluid coke, said fluid coke having been produced by contacting a heavy petroleum oil coking charge stock at a coking temperature with a body of fluidized coke particles in a reaction zone wherein the oil is converted to product vapors and carbonaceous solids are continuously deposited on the coke particles, removing product vapors from the coking zone, heating a portion of the coke from the coking zone in a heating zone to increase the temperature of said fluidized particles, returning a portion of the heated coke particles from the heating zone to the coking zone and withdrawing coke product particles, placing said mixture on a heated pattern, forming thereby a thin hardened layer of said composition in the form of said pattern, and recovering from said pattern a shell mold.

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