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CORE MOLDING COMPOSITION

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The present invention relates to the manufacture of cores for casting metal and in particular it relates to improved cores used in the manufacture of hollow castings. Specifically, it concerns the use of a core oil comprising a mixture of a polymer oil, resin and vegetable oil.

Because the finely divided matter used in the preparation of cores has no natural binding property, it is necessary to employ a binder or core oil to hold the particles together. Considerable skill is necessary to prepare satisfactory cores. The binder must mix well with the inert material so that each particle is coated and the core has a uniform density, but it must not create a sticky condition which would gum up the core molding boxes nor should it cause the core to swell or crack in baking or in storage. It should not absorb moisture from the atmosphere after it has been set in the mold waiting for the metal to be poured. A satisfactory binder must impart sufficient bond strength to the core before it is baked to permit manual handling, and permit easy removal of the sand core from its mold prior to baking.

During baking, the binder should oxidize and/or polymerize to yield a core having sufficient tensile strength to withstand the weight of metal when the casting is poured and strong enough to resist ordinary handling in the foundry, both before and after baking. It should decompose, or burn out, after the metal is poured, but not until the metal has hardened sufficiently so as not to lose its shape. With a proper binder, when the casting is cooled, the inert ingredients in the core can be easily broken up and shaken free from the casting.

In the prior art, it has been common to use various compositions comprising linseed oil, fish oil, and other fatty, vegetable and animal oils, along with modifiers of various types as the binder in the preparation of cores for metal castings. These oils were chosen because they combine with oxygen in the air during the baking step and are converted into a strong binder cementing the grains of sand to each other and yielding a firm, hard core. Commonly, such cores are baked with an optimum amount of the core oil binder, the preferred compositions having the property of polymerizing to a moderate extent to serve as a binder. Baking is conventionally carried out in a ventilated oven at moderately high temperatures, e. g. between 350 and 600° F. At such temperatures, volatile constituents of the core oil or binder are removed but the residue polymerizes or thickens without undue charring to bind the sand and into a firm structure. It is a common practice in the art to add a soap of iron, lead, manganese or cobalt to the binder to accelerate baking.

When the actual casting takes place, the temperature of the metal is quite high, ranging from 1200° F. for aluminum to approximately 3000° F. for iron. The temperature of the metal and the nature of the binder are preferably such that the binder breaks down as the metal begins to cool and assumes the configuration of the core. The sand can then be freely shaken out of the cast metal product after the metal has solidified.

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It has now been discovered that mixtures of a petroleum resin, a clay treated polymer, and linseed oil make outstanding core oils.

The petroleum resin is prepared as follows: A steam cracked distillate boiling largely in the range of about 77 to 86° F. is exposed to a thermal soaker wherein the dimers of cyclic diolefins are converted to the monomeric form. The thermally soaked product is then distilled to remove any cyclopentadiene dimers, the cycloienes being removed as a concentrated stream from the lower portion of the distillate tower. The undimerized portion, C₅-C₈, is passed overhead to a receiver and reflux drum where part is removed to the upper part of the fractionator as reflux. This C₅-C₈ portion is then sent to the reaction zone where it polymerizes in the presence of a Friedel-Crafts catalyst, such as aluminum chloride, at a temperature between -40 and 158° F. The polymer is then passed through a catalyst removal zone and thence to a steam distillation tower. Here the C₅-C₈ is removed overhead and the crude resin fraction is passed to another distillation zone, from which a liquid polymer stream is removed overhead and the finished resin is removed as a bottoms product.

The petroleum resin generally has a softening point between about 158 and 230° F., a Wijs iodine number between about 92-119, and intrinsic viscosity between about 0.037 and 0.120 and a light to medium amber color.

The clay treated polymer oil is prepared in a clay treating unit which consists of a furnace having two individual circuits, one of which is used to preheat the feed and the other to supply heat to the fractionating tower which separates the polymer from light and heavy naphtha, and a drum charged with about 20 tons of 8 to 15 mesh Attapulugus clay. The highly olefinic feed stream consists of a mixture of depentanized distillate from an isoprene fractionator unit and debutanized bottoms from a steam cracking unit. It boils between about 50 to 500° F. and contains about 10 to 25% conjugated diolefins, 40 to 60% olefins, 20 to 40% aromatics, and 2 to 5% paraffins. The liquid feed stream is generally preheated to about 250 to 300° F. and passed downwardly through the clay drum. A temperature rise of about 30 to 50° F. occurs in the clay bed as a result of the exothermic reaction. The treated distillate leaving the clay drum is transferred to a fractionating tower which separates the clay treated polymer from light and heavy naphtha. A stripper in the bottom of the tower removes any light hydrocarbons that may be mixed with the polymer.

The clay treated polymer oil generally has a Staudinger molecular weight between about 200 and 1000 and a Wijs iodine number between about 240-320, preferably about 260. It has about 82 to 95% by weight non-volatile matter (ASTMD-154-43) and an ash of about 0.3 to 0.4 wt. percent. The polymer's viscosity at 210° F. is usually about 100 to 300 seconds, and preferably about 156 seconds, in a Saybolt Universal viscometer. The maleic anhydride and Gardner Diene numbers are about 109 and 19, respectively. It boils between about 400 and 1000° F., having 5% and 95% points at about 500 and 910° F., respectively. The flash point should be between about 190 and 300° F. Its API at 60° F. is between about 6 and 14.

The quantity of clay treated polymer employed in the core oil, on a NVM basis, should be between about 20 and 80 wt. percent, and it is preferred to use between about 30 and 40 wt. percent. In the case of petroleum resin, it should be present in an amount between about 20 and 80 wt. percent, and preferably between about 30 and 40 wt. percent. An especially desirable combination of these two polymers is where there is about 33 wt. percent

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clay treated polymer and 33 wt. percent petroleum resin. In all of these oils the balance of the NVM in the formula is made up with raw linseed oil, e. g. 20 to 80 wt. percent, preferably 30 to 40 wt. percent. The whole core oil comprises about 30 to 70 wt. percent volatile matter and about 30 to 70 wt. percent non-volatile matter. The volatile portion generally comprises a mineral hydrocarbon solvent. The solvent should have a boiling range between about 130 and 500° F. and consist of about 15 to 98 vol. percent aromatics, 0 to 45 vol. percent naphthenes and 0 to 45 vol. percent paraffins, and have a kauri-butanol value between about 35 and 130. It is preferred to use core oils containing between about 40 and 60 wt. percent of a hydrocarbon solvent boiling between 200 to 400° F.

The finely divided inert solid (about 40 to 200 mesh) which makes up the major proportion of the core must be a material which has a relatively high level of strength or structure. Sand is the most common material employed because of its availability and low cost. However, other substances such as coke, silica, alumina, etc. may be used. An excellent source of these finely divided materials is the spent catalysts used in a number of refining operations.

In addition to the core oil, the core mixture may include oxidation promoters, such as iron, cobalt or manganese naphthanates; polymerization catalysts, such as benzoyl peroxide, ditertiary butyl peroxide and combinations thereof may be employed.

In the preparation of the core, the ingredients are mixed and kneaded together to produce a uniform composition. It is imperative that the liquids coat the surface of the finely divided matter to insure its adhesion after it is baked. For example, 100 parts by weight of sand is mixed with between about 0.25 and 5.0 parts by weight (NVM) of core oil containing linseed oil, petroleum resin and clay treated polymer, preferably between 0.75 and 1.50 parts by weight, and between about 1 and 5 parts by weight of water. If the total weight of the core oil is to be used, then about 0.5 to 10 parts by weight of oil must be employed since about 40 to 60% of the core oil is composed of a solvent. Small amounts of drying agents may be added, for example, between about 0.01 and 2.0 parts by weight. The resulting composition is then molded into the desired shape and baked from about a few minutes, e. g. about 30 minutes, up to about 300 minutes at an elevated temperature, e. g. between about 350 and 450° F. During the baking operation, the polymers and linseed oil interact to form a substance having outstandingly high tensile strength properties. It is also possible, in the case of certain cores, to use an

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The one part by weight of core oil in the above formula refers to the amount of non-volatile matter (NVM) in the oil and not the total composition. This takes into account any differences in the amount of solvent in the various oils and places them all on the same basis.

EXAMPLE 1

Cores made according to the general formula were prepared using each of the following substances, linseed oil, CTLA polymer, having a viscosity of 154 SSU at 210° F. and an iodine number of 260, and PRLA resin having a softening point of about 204° F. The two last named substances contained Varsol which is a solvent having the following properties:

Boiling range:
Initial -----°F. 322
Final -----°F. 404
Specific gravity, 60/60° F.----- 0.800 to 0.810
Aromatics, vol. percent----- 25 to 35
Naphthenics, vol. percent----- 34 to 40
Paraffinics, vol. percent----- 30 to 36
Kauri-butanol value----- 38 to 44

Each core was molded and baked at 400° F. for predetermined periods of time. The results are set forth in Table I.

Table I

Core	NVM, Wt. Percent	Viscosity, SSU @ 100° F.	Tensile Strength, p. s. i.—After Each Baking, min.			
			30	90	120	150
Petroleum resin (50% Varsol)-----	50	158	-----	69	-----	69
Clay Treated Polymer 80%-----	182.7	-----	70	87	85	-----
Varsol 20%-----			51	279	-----	283
Linseed Oil-----	100	13.3	-----	-----	-----	-----

1 NVM of polymer.

The above data show that neither the clay treated polymer or the petroleum resin, when used alone, are satisfactory core oils.

EXAMPLE 2

A core was prepared according to the general formula wherein the oil employed was a combination of PRLA resin, CTLA polymer and linseed oil. This core was evaluated for its tensile strength after various periods of baking. The results are set forth in Table II.

Table II

Core Oil	Wt. Percent	NVM (Wt. cent)	Baking Temp., ° F.	Viscosity, SSU @ 100° F.	Tensile Strength, p. s. i.—After Each Baking, min.		
					30	90	150
Petroleum Resin (40% Varsol)-----	53.2	63.7	400	132	73	248	319
Clay Treated Polymer (82.7%)-----	25.6						
Linseed Oil-----	21.2						

open flame for from a few minutes up to about 10 minutes instead of baking the core.

The following examples are given so that the present invention will be more clearly understood. The formula set forth below was employed in the preparation of each of the cores used in the examples:

Ingredients:	Parts by weight
AFS standard test sand-----	100.0
Core oil-----	1.0
Water -----	3.0

The results show that a combination of the petroleum resin, the clay treated polymer and linseed oil makes a more effective core oil than any one of the ingredients alone. Furthermore, it is important to note that the core's tensile strength continues to substantially increase with each successive baking time. This is an important and unexpected feature of the present invention. This also shows that the core oil is not burning out during the baking operation. This is an important feature because in the manufacture of these cores it is not uncommon to leave

these cores overnight in an oven to cool. When this is done there is a possibility that part, and sometimes all, of the core oil is burned out. Thus the present invention tends to avoid this undesirable result.

Resort may be added to many modifications and variations of the present invention without departing from the spirit of the discovery or the scope of the appended claims.

What is claimed is:

1. A core oil composition composed of about 30 to 70 wt. percent of non-volatile matter which comprises about 20 to 80 wt. percent of a hydrocarbon polymer oil boiling between about 400 and 1000° F., having an iodine number between about 240 and 320 and a Staudinger molecular weight between about 200 and 1000, about 20 to 80 wt. percent of a petroleum resin having a softening point between about 158 and 230° F., an iodine number between about 92 and 119 and an intrinsic viscosity between 0.037 and 0.120 and 20 to 80 wt. percent of vegetable oil, and about 70 to 30 wt. percent of volatile matter comprising a hydrocarbon solvent boiling between about 130 and 500° F. and having a kauri-butanol value between about 35 and 130.

2. A core oil composition according to claim 1 in which the amount of non-volatile matter is between 40 to 60 wt. percent and the amount of volatile matter is between 60 and 40 wt. percent.

3. A core oil composition according to claim 1 in which the vegetable oil is unsaturated.

4. A core oil composition according to claim 1 in which the vegetable oil is linseed oil.

5. A core oil composition having the following formula:

	Wt. percent
Non-volatile matter-----	40 to 60
Hydrocarbon-polymer oil having an iodine number between 240 and 320 and a Staudinger molecular weight between 200 and 1000-----	30 to 40
Petroleum resin having a softening point between about 158 and 230° F., an iodine number between 92 and 119 and an intrinsic viscosity between 0.037 and 0.120-----	30 to 40
Linseed oil-----	Balance
Volatile matter comprising a hydrocarbon solvent boiling between 130 and 500° F. and containing between 15 and 98 vol. percent aromatics -----	60 to 40

6. A core molding composition which comprises 100 parts by weight of a finely divided solid and about 0.25 to 5 parts by weight of a binder comprising 20 to 80 wt. percent of a hydrocarbon polymer oil boiling between about 400 and 1000° F., having an iodine number between about 250 and 320 and a Staudinger molecular weight between about 200 and 1000, 20 to 80 wt. percent of a petroleum resin having a softening point between about 158 and 23° F., an iodine number between 92 and 119

and an intrinsic viscosity between 0.037 and 0.120 and about 70 to 30 wt. percent of volatile matter comprising a hydrocarbon solvent boiling between about 130 and 500° F. and having a kauri-butanol value between about 35 and 130 and the balance linseed oil.

7. A core molding composition according to claim 6 in which the quantity of binder is between 0.75 and 1.5 parts by weight.

8. A core molding composition according to claim 6 in which the finely divided solid is sand.

9. A core molding composition according to claim 6 in which the finely divided solid is fluid coke.

10. A process for preparing a core suitable for use in the manufacture of hollow castings which comprises mixing 100 parts by weight of a finely divided solid with between about 0.5 and 10 parts by weight of a core oil composed of about 30 to 70 wt. percent of non-volatile matter which comprises about 20 to 80 wt. percent of a hydrocarbon polymer oil boiling between about 400 and 1000° F., having an iodine number between about 240 and 320 and a Staudinger molecular weight between about 200 and 1000, about 20 to 80 wt. percent of a petroleum resin having a softening point between about 158 and 230° F., an iodine number between about 92 and 119 and an intrinsic viscosity between 0.037 and 0.120 and 20 to 80 wt. percent of vegetable oil, and about 70 to 30 wt. percent of volatile matter comprising a hydrocarbon solvent boiling between about 130 and 500° F. and having a kauri-butanol value between about 35 and 130, molding the resulting mixture, baking the resulting molded mixture for from a few minutes up to 300 minutes at a temperature between about 350 and 600° F. and recovering a core.

11. A process according to claim 10 in which the baking step is replaced by heating the molded mixture with an open flame for from a few minutes up to about 10 minutes.

12. A process according to claim 10 in which between about 1 to 5 parts by weight water is admixed with the finely divided solid and the core oil.

13. A process according to claim 10 in which the finely divided solid is sand.

14. A process according to claim 10 in which the finely divided solid is fluid coke.

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