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CORE OIL COMPOSITIONS CONTAINING ORGANIC FIBERS

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This invention relates to foundry cores and molds and to the method for making such cores and molds and, more particularly, to binders and core oils having improved green strength used in the production of cores and molds.

In the casting of metals, molds are prepared of sand or other core materials such as zirconia, alumina, fluid coke or the like bonded together by a binder. The sand and binder are shaped in the form desired and the form is then baked to develop strength in the core so that it can withstand handling during the casting operation without deforming or breaking. The core should have sufficient green strength to retain its form before baking and sufficient tensile strength during the casting operation, but should not be so hard as to be difficult to break away and remove from the finished casting. Thus, the most desirable core material is that which can be baked to a given form in a reasonably short period of time and, also, will not lose its strength under extended heating.

Core oils used as binders to bind the mineral core-forming material should coat the sand with a thin film and should bind the sand grains together and provide sufficient green strength in the formed core. Core oils of the type known heretofore generally have been produced from drying oils such as linseed oil, perilla oil, China wood oil, tung oil, etc. Such heat-polymerizable oils are hardened by oxidation and polymerization through double bonds in the highly unsaturated oil when the oil is exposed to elevated temperatures.

Usually, in approximately equal amount of water, together with a water-dispersible adhesive such as starch or cereal must also be added to the sand to impart green strength; i.e., to make the sand stick together before baking to give a good impression of the pattern and to permit the removal of the core from the pattern without collapse prior to baking.

These drying or semi-drying oils possess several deficiencies limiting their desirability as binders in the production of cores. Because the oils polymerize and develop strength by oxidation and this oxidation takes place slowly, extended exposure of the cores to elevated temperatures in baking ovens is necessary. Furthermore, if the cores are inadvertently left in the oven after the optimum amount of polymerization has taken place, oxidation continues causing degradation of the binder and loss of strength in the core. Even after optimum amount of baking, however, cores utilizing such binders do not have the desired strength, and this is demonstrated by the fact that reinforcing wires are often used in such cores to provide additional mechanical strength.

Many of the disadvantages of ordinary core oils are overcome by the use of epoxy core oils prepared from epoxidized oils. Generally, the epoxy core oils which provide the improved benefits over the ordinary core oils comprise adducts of ethylenically unsaturated hydrocarbons or derivatives thereof and polymers from polyepoxides and lactams. The strength of the polymer and the ease with which the polymer is formed are increased by the presence of a small amount of a polyamine. These epoxy core oils possess a marked affinity for core materials such as sand, fluid coke, alumina, zirconia, etc., and appear to coat the mineral particles with a thin film of the binder composition which, when baked, provide

a high degree of tensile strength in the core. The epoxy core oils are highly effective binders and can be used in very small amounts in the core oil composition.

While epoxy core oils are superior to the ordinary core oils, they do possess some drawbacks. For example, epoxy core oils are most effective in the absence of moisture. Accordingly, the water dispersible adhesives such as water-cereal mixtures which are used to control the green strength of ordinary core oil should not be used when the epoxy core oils are employed.

It is, accordingly, an object of this invention to provide core oil compositions which do not possess the aforementioned deficiencies of core oils known heretofore and which cure more rapidly to give stronger cores less subject to heat degradation than those previously known.

Another object of the invention is the provision of an improved, inexpensive core oil composition which possesses a substantial affinity for the mineral core materials and which can be cured in a very short period of time to produce a core having a substantial amount of mechanical strength.

Still another object of the invention is to provide metal casting cores having a high degree of strength without the necessity for utilizing reinforcing wires.

Another object of the invention is the provision of an improved method for manufacturing inexpensive, high-strength cores which are not subject to deterioration and loss of tensile strength.

A still further object of the invention is to provide sufficient green strength to make the sand cores stick together sufficiently to give a good impression of the pattern and to permit the removal of the core therefrom without collapse prior to baking.

Additional objects, if not specifically set forth herein will be readily apparent to those skilled in the art from the detailed description of the invention which follows.

In most foundry applications, a green core strength of at least 0.70 p.s.i. is required and frequently a green strength as high as 1.50 p.s.i. is needed. It has now been discovered that the green strength of epoxy core oil compositions can be effectively controlled by adding to the sand-core oil mixture, a low concentration of organic fibers.

In general, the low green strength of epoxy core oil mixtures can be increased up to three times the original value by the addition of certain types of organic fibers which have good thermal stability at the baking temperature of the cores, which is usually 350–600° F., yet which are thermally unstable so as to decompose at temperatures usually in excess of 1,000° F. so as to enable the cores to be disintegrated and removed from the castings.

More specifically, the green strength of epoxy core oils can be increased and controlled by adding to the sand-core oil mixture a low concentration of organic fibers such as cotton linters, leather fibers (both mineral and vegetable-tanned), wood pulp fibers, rag fibers, kapok fibers, peanut shell fibers, corn cob fibers, jute fibers, hemp fibers, sisal fibers, as well as wool, silk, nylon, polyester, polyacrylonitrile, polyethylene, polypropylene, polyurethane, polyurea fibers, etc. While the length of the fibers may vary, they should not be too long as they may tend to interfere with the mixing of the oil and sand. In general, the length of the fibers may vary from 1 to about 10 millimeters. Fibers of from about 3 millimeters to about 6 millimeters are preferred. The use of the organic fibers produces a most unusual and unexpected result. This is especially so since it was found that all of the additives (cereal, bentonite, clays, starch, etc.) which are customarily used with conventional core oils to produce high green strength fail to produce satisfactory cores when an epoxidized core oil was employed.

The organic fiber additives that are used in the practice of the present invention may be incorporated into the sand composition in any desired manner. Thus, the organic fibers may be directly mixed or mulled into an epoxy core oil containing sand. Also, it is possible to incorporate the fibers by dispersing them in the core oil that is used as a binder for the sand prior to the mixing of the binder with the sand to form the foundry core composition. The core oil bonded sand compositions can be cured and baked after fabrication in the usual manner, as by subjecting them to heat at elevated temperatures or baking in an oven according to the conventional technique. Usually, the quantity of the organic fiber additive that is incorporated into the core oil-sand composition is an amount between 0.1 and 200 percent by weight based on the weight of the core oil in the composition and, more particularly, an amount between 10 and 150 percent by weight.

The epoxy core oil bonded compositions which contain the organic fibers in accordance with this invention may be fabricated into excellent foundry cores having improved physical properties, especially high green strength, at any given core oil content as compared to identical compositions except for containing the additive. The cores and molds manufactured from the instant composition possess excellent release characteristics from a solidified casting. The collapsibility after the casting has been finished is quite satisfactory.

The epoxy oil-sand compositions containing the organic fibers have good flowability, allowing the composition mixture to flow into hard-to-get-at cavities. The compositions may be rammed or blown easily into the particular voids to produce a good, strong structure. Any ordinary core material may be utilized in this invention. Ordinarily, sand or other refractory material such as zirconia, alumina, fluid coke or the like may be employed. Of course, the fineness of the core material may vary depending upon the intended use, and it is not necessary in the practice of this invention to employ clean sand.

The epoxy core oils which are suitable in the instant invention can be selected from a wide range of epoxy polymers. Normally, any core oil containing non-terminal epoxy polymers is satisfactory. Since the use of epoxy polymers in core oils is a fairly recent advancement in the art, it is desirable to set forth in detail the specific class of epoxy core oils which give exceptionally good results when employed with the organic fibers. Generally, compositions providing the benefits of this invention, in conjunction with the organic fibers, comprise as the major ingredient an adduct of an ethylenically unsaturated hydrocarbon or derivative thereof and a minor amount of polymers formed from polyepoxides and lactams. The strength of the polymer and the ease with which the polymer is formed are increased by the presence of a small amount of a polyamine.

More specifically, the core oils which can be employed in this invention are made up primarily of adducts of aliphatic unsaturated dicarboxylic acid anhydrides and ethylenically unsaturated hydrocarbons, including ethylenically unsaturated higher fatty acids and esters thereof. Diels-Alder type adducts prepared from ethylenically unsaturated dicarboxylic acid anhydrides such as maleic anhydride and dienes can be used, but in the interest of economy maleinized fatty acid and maleinized oils are preferred herein. Embodied in this adduct is the polymer prepared from the polyepoxide, lactam, and a polyamine. Although the polymer can be employed without any adduct to produce a highly desirable, high-strength binder, it is preferred, inasmuch as only a very small amount of the polymer is required to give great strength to the core, to use the prereacted adduct as the major component in the core oil.

The adduct is prepared from a lower aliphatic dicarboxylic acid anhydride such as maleic anhydride, chloromaleic anhydride, or citraconic acid anhydride and an unsaturated organic composition. Maleic anhydride is the preferred anhydride. The unsaturated organic composition which is combined with the anhydride to form the adduct may be any hydrocarbon, fatty acid, or fatty acid ester having carbon-to-carbon double bonds, free of benzenoid unsaturation. While such dienes as butadiene and isoprene can be employed to form Diels-Alder type adducts, it is preferred that unsaturated compositions such as unsaturated higher fatty acids and unsaturated higher fatty acid esters be employed in preparing the adduct. Nonconjugated, unsaturated fatty acids and esters thereof form maleinized fatty acids and maleinized oils with maleic anhydride. Maleinization provides a means for inserting free acid groups in the middle of unsaturated ester chains plus increasing the functionality of the fatty acid or ester. Maleinization is carried out by heating the conjungated or nonconjugated, unsaturated fatty acids and/or esters with the anhydride at a temperature above about 200° C.

Such higher fatty acids and fatty acid esters as myristoleic acid, lauroleic acid, palmitoleic acid, oleic acid, linoleic acid, linolenic acid, eleostearic acid, arachidonic acid, dimer acids, tall oil header cut and other 10–22 carbon acids and esters thereof may be employed in preparing the adduct. The naturally-occurring animal, vegetable, and marine oils such as soybean oil, linseed oil, safflower oil, perilla oil, menhaden oil, as well as mixtures of fatty acids derived from such glyceride oils, may also be used as the source of ethylenically unsaturated material in the preparation of the adduct. "Acidulated foots" provide an additional inexpensive source of fatty acid. These "foots" are attained by acidulating soapstock produced as a by-product in the refining of glyceride oils with alkali. The soapstock or residue from alkali refining is boiled with sulfuric acid to provide "acidulated foots" composed primarily of fatty acids in the free form. Acidulated foots may contain more than about 85% fatty acids. Acidulated corn oil foots, acidulated soybean oil foots, acidulated linseed oil foots, and acidulated cottonseed oil foots contain appreciable amounts of unsaturated fatty acids.

The polymer which forms a minor amount of the core oil composition comprises a copolymer of an oxirane-containing fatty acid ester having an average of more than one oxirane group per molecule and a lactam, usually caprolactam, and additionally contains polymino radicals. The polymer is prepared from a polyepoxide and about 2–50% of caprolactam based on the weight of the oxirane-containing composition and about 1–50%, based on the weight of the oxirane-containing composition, of the polyamine. Preferred quantities of caprolactam are around 2–10% based on the weight of the oxirane-containing composition, while preferred quantities of the polyamine are around 1–20% based on the weight of the oxirane-containing composition.

Polyepoxides which are condensed with the lactam include generally, those oxirane-containing compositions having more than one epoxy group per molecule and includes esters of oxirane-substiuted higher fatty acids, particularly dihydric and other polyhydric alcohol esters of such fatty acids and mixtures thereof. Glyceride esters of oxirane-containing higher fatty acids substantially free of terminal oxirane groups are very desirable as the source of oxirane groups. Synthetic glycerides such as epoxidized triolein, epoxidized trilinolein, and epoxidized trilinolenin, and mono- and diglycerides of such epoxidized fatty acids are very satisfactory. Naturally-occurring animal, vegetable, and marine triglycerides when epoxidized to contain more than one oxirane group per molecule represent a convenient and economical source of epoxidized esters.

The more highly epoxidized glycerides; that is, epoxidized perilla oil or epoxidized linseed oil, when substantially completely epoxidized, are characterized by oxirane oxygen content of more than about 7% and may, in some cases, analyze at 9.5% oxirane oxygen and above. The high functionality of such compositions permits the

production of harder copolymers of higher tensile strength in a shorter period of time than where less highly epoxidized materials are employed.

Epoxidized tallow, epoxidized cottonseed oil, epoxidized soybean oil, epoxidized menhaden oil, epoxidized sardine oil, epoxidized sprem oil, epoxidized safflower oil are a few of the many epoxidized naturally-occurring glycerides which can be used in forming the copolymer. The fatty acids derived from these naturally-occurring glycerides when esterified with lower aliphatic, monohydric, dihydric, trihydric, tetrahydric, and pentahydric and hexahydric alcohols results in compositions which are also a desirable source of the polyepoxide. Examples of such alcohols which may be esterified with epoxy fatty acids to form suitable esters include lower glycols, glycerol, erythritol, mannitol, pentaerythritol, and sorbitol. Aliphatic polyhydric alcohol esters of oxirane-containing fatty acids of 10–22 carbons generally are employed in preparing copolymers having high strength.

The polyamine reactant utilized in forming the copolymer can be any primary or secondary aliphatic or aromatic amine having more than one amino group. Alkylene polyamines such as the diamines, triamines, tetramines, pentamines, and hexamines are included in the definition of the polyamine reactant. Specific alkylene polyamines include ethylene diamine, trimethylene diamine, pentamethylene diamine, hexamethylene diamine, diethylene triamine, triethylene tetramine, tetraethylene pentamine, and long-chain polyamines such as the N-alkyl alkylene polyamines wherein the alkyl substitution comprises a long-chain alkyl group of 10–22 carbons. Aromatic polyamines include o-phenylene diamine, m-phenylene diamine, o-tolidine, 2,4-tolidine, 2,4-tolylene diamine, 1,4-diamino naphthalene, and other aromatic polyamines free of interfering substituents.

While, as has been noted previously, the core oil can be made up exclusively of the polymer, it is preferred that this component of the binding agent be present in a minor amount and the maleic anhydride adduct be present in a major amount. As little as one percent of the polyepoxide-lactam polymer based on the weight of the binder, the remainder being the adduct, provides a highly effective core oil. As the amount of the polymer in the core oil composition is increased, the strength of the core increases. A desirable core oil which can, in combination with the sand, be baked in a reasonably short period of time to provide a core of substantial mechanical strength is made up of 5–50% by weight of the polymer. The proportions of the polymer to the prereacted maleinized unsaturated material can be adjusted by those skilled in the art to satisfy the requirements for a given casting or molding operation.

The core oil possesses a high degree of adherence to the sand particle and flows in and around the particles, forming a film enveloping the particles. Good mechanical strength in the core is provided by small amounts of the binder and, for this reason, the core oil is very economical. Amounts of core oil as low as 0.5% based on the weight of the mineral core material results in cores having a high degree of mechanical strength and amounts up to around 4% based on the weight of the mineral core materials provide some advantages. Larger amounts, while operable, are uneconomical.

A number of other binder materials can be added to the epoxy core oils, if desired. Among such materials is included polymers obtained by contacting clay with a highly olefinic hydrocarbon stream. Such a polymer is CTLA, which can be obtained from the stream cracking of gasoline at high temperatures and low pressures, e.g. at a temperature in the range of 1100° F. to 1300° F. This product is a very viscous, semisolid, highly unsaturated plastic material. The product can be derived in various ways from gasoline refining processes; one preferred method is to filter the gasoline through clay and then to extract the polymer deposited on the clay with a light solvent, such as butane, propane or the like, after which the solvent, of course, is evaporated and the residue used as a supplemental binder.

The following examples are presented to illustrate the invention. It will be understood that these examples are illustrative and are not to be taken in any manner as limiting the invention as defined in the apended claims.

Example I

The copolymer reactants are mixed in a 2-liter flask. The reactants are:

	Grams
Epoxidized linseed oil (oxirane 9.0%)	1200
Caprolactam	48
Triethylene tetramine	19.2

The reactants are mixed and the flask is evacuated with a water aspirator while the mixture is heated in a boiling water bath for 2 hours. The reaction mixture is then cooled to room temperature and 14.4 grams of trioxymethylene is added. The trioxymethylene is not necessary, if the core oil is to be used within about 2 weeks. It is employed as a viscosity stabilizer and prevents jelling on long standing. The polymer reaction product is then warmed until the trioxymethylene is dissolved. 534 grams of maleic anhydride, 4,130 grams of linseed foots and 5,200 grams of a CTLA polymer (Enjay) are heated at 204° C. for about 4 hours and then cooled to room temperature. This mixture is then added to the polymer and the entire mixture is agitated until a homogeneous mixture is obtained.

A core is prepared by adding 3 grams of the epoxy core oil mixture prepared above to 300 grams of a dry, foundry grade silica sand and mixed until uniform. An A.F.S. standard cylindrical sand core was prepared and its green strength determined by the standard procedure using the Dietert Universal sand testing machine. The core had a green strength of 0.53 p.s.i.

Example II

A core was prepared by using the same epoxy core oil mixture as was employed in Example I. 3 grams of this mixture was added to 300 grams of dry silica foundry sand and the system mixed until uniform. 1.0 gram of cotton linters (No. 2) was added and the mixture again agitated until uniform. A standard core was prepared and its green strength determined. The resulting green strength was 0.80 p.s.i.

Example III

Another core was prepared using the same reactants and procedure as employed in Example II, except 2.0 grams of bark-tanned leather fibers was employed in place of the cotton linters. This core had a green strength of .85 p.s.i.

Example IV

Example II was repeated except 4 grams of cotton linters was employed. The green strength of the core was 1.52 p.s.i.

Example V

A core was prepared by using the same epoxy core oil mixture as was employed in Example I. 6 grams of this mixture was added to 300 grams of dry zirconia sand and the system mixed until uniform. 0.006 gram of silk fibers was added and the mixture again agitated until uniform. A standard core was prepared and its green strength determined. The resulting green strength was substantially higher than that of the core prepared in Example I.

Example VI

A foundry core was prepared using the same core oil mixture as was used in Example I. 4 grams of this mixture was added to 300 grams of foundry sand and the system mixed until uniform. 8 grams of wood pulp fibers was added and the mixture again agitated until uniform. A standard core was prepared and its green strength determined. The resulting green strength was more than

twice as great as that of the control core of Example I, which contained no fibers.

The binder used in this invention mixes well with the sand and produces cores of uniform density. The binder does not create a sticky condition when in the core molding boxes nor do the cores swell or crack in baking or during storage. Most of all the binder composition imparts sufficient green strength before it is baked to permit manual handling.

Cores produced by the method of this invention have sufficient tensile strength to withstand the weight of metal when the casting is poured. The binder decomposes when the metal is poured and after cooling, the sand core can be easily broken up and shaken free from the casting.

It is apparent that many modifications and variations of the invention as hereinbefore set forth may be made without departing from the spirit and scope thereof. The specific embodiments described in the examples are given by way of illustration only and the invention is limited only by the terms of the appended claims.

I claim:

1. A composition for producing foundry cores and molds which comprises: sand, an epoxy core oil comprising the polymeric reaction product of an epoxidized oil, an aliphatic lactam, and a polyamine curing agent in conjunction with a maleinized, unsaturated higher fatty acid and oragnic fibers, having a length of at least about one millimeter.

2. The composition of claim **1** wherein the organic fibers are selected from the group consising of cotton linters, leather fibers, wood pulp fibers, rag fibers, kapok fibers, peanut shell fibers, corn cob fibers, coconut husk fibers, jute fibers, hemp fibers, sisals fibers, wool, silk, nylon, polyester, polyacrylonitrile, polyethylene, polypropylene, polyurethane and polyureau fibers.

3. A composition for making foundry cores and molds having acceptable green strength comprising: sand in admixture with a binder comprising a core oil containing the polymeric reaction product of an oxirane-containing higher fatty acid ester, an aliphatic lactam and a polyamine curing agent, and organic fibers having a length of at least one millimeter.

4. The composition of claim **3** wherein said core oil further contains an aliphatic dicarboxylic acid anhydride adduct of an organic compound containing non-aromatic, ethylenic unsaturation.

5. The composition of claim **4** wherein said lactam is caprolactam and said anhydride is maleic anhydride.

6. A non-deforming core having acceptable green strength comprising: an admixture of a refractory core material, a core oil, and organic fibers, said core oil containing the polymeric reaction product of an oxirane-containing higher fatty acid ester, an aliphatic lactam and a polyamine curing agent.

7. A method for manufacturing metal casting cores of high green and tensile strength comprising: mixing a refractory core body material with a small amount of a core binder comprising a mixture of an aliphatic dicarboxylic anhydride adduct and the polymeric reaction product of an oxirane-containing higher fatty acid derivative containing more than 7% oxirane oxygen, an aliphatic lactam and a polyamine curing agent and an admixture of organic fibers, distributing said binder throughout said core material, and forming said mixture in the desired shape.

8. The method of casting metals which comprises mixing a core body material with a refractory minor portion of a core binder comprising: a mixture of an aliphatic dicarboxylic anhydride adduct and the polymeric reaction product of an oxirane-containing higher fatty acid ester, an aliphatic lactam, and a polyamine curing agent, and an admixture of organic fibers having a length of at least about one millimeter, forming a mold of the resulting composition, and casting the metal in the resulting mold.

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UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

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Robert J. Johnson

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 1, line 48, "the" should read -- these --. Column 2, line 7, "water dispersible" should read -- water-dispersible --. Column 4, line 22, "arachidionic" should read -- arachidonic --; line 45, "polymino" should read -- polyamino --; line 56, before "generally" insert a comma; lines 57 and 58, "includes" should read -- include --; line 58, "substiuted" should read -- substituted --. Column 5, line 6, "sprem" should read -- sperm --. Column 6, line 6, "apended" should read -- appended --. Column 7, line 7, after "all" insert a comma; line 35, "polyureau" should read -- polyurea --. Column 8, line 19, before "core" insert -- refractory --; same line 19, before "minor" cancel "refractory".

Signed and sealed this 14th day of October 1969.

(SEAL)
Attest:

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