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FOUNDRY CORE OR MOLD AND METHOD
OF MAKING SAME

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This invention relates to foundry structures, such as cores and molds, and more particularly to a new and improved bonding agent therefor, and methods of making such structures.

The practice in making foundry cores for use in the production of castings has been to mix sand, substantially free of clay, or other comminuted refractory material with a suitable bonding agent, tempering with just sufficient water to make a workable intimate mixture, then ramming, blowing or forcing into core boxes and thus making cores therefrom. Cores thus produced may be used green; i. e., as rammed, but generally they are dried by baking in core ovens at temperatures ranging from about 250° F. to about 650° F.

In the preparation of molds, a comminuted refractory material comprising a mixture of sand and some clay-like substance is ordinarily used. Organic binders up to about 1% are generally added to the mixture to give increased dry strength. A suitable amount of tempering water is added to the molding mixture to facilitate the forming of the mold structure and the structure may be used green, but where greater strength is desired, the structure is preferably oven or torch dried.

A supplementary treatment of portions or all of the surface of foundry structures with sprays or pastes comprising the same incorporated bonding agent, or of different bonding agents, for the purpose of imparting special surface characteristics to foundry structures, is a well-recognized practice in the art of making foundry structures.

The essential function of a bonding agent in foundry structures is to impart dry strength and hardness to the structure to withstand handling and the erosive action of the molten metal that comes in contact with it during the casting operation. A satisfactory structure should disintegrate readily after the metal has been cast so as to be readily removable therefrom. Also, the bonding agent should be such that the comminuted refractory material may be easily recovered for re-use in a subsequent operation. Resistance to moisture is another important characteristic of a good foundry structure bonding agent. Surface bonding agents function additionally to present a smooth surface to the metal and also to insure against escape of sand and other particles from the foundry structure into the molten metal.

The bonding agents employed in the art for use in making foundry structures have not proven entirely satisfactory for different reasons. Rosin,

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powdered for use in the solid state in making foundry structures, reverts or solidifies into one solid mass upon standing. Furthermore, some of the constituents of so-called core oils crystallize out of solution upon standing. Cereals, starches, glue, and the like, putrefy on standing and give off large quantities of gases during baking and also absorb moisture from the air. Vegetable oils require a high baking temperature with sufficient oxygen to develop their bonding power. Foundry pitch requires baking temperatures of about 600° F. or higher and cores incorporating it are difficult to remove in the cleaning operation. Molasses and waste sulfite pulp liquor migrate to the surface of the structure in the baking operation forming a strong, hard film which is impervious to gases generated in the casting operation.

Now, in accordance with this invention there is provided the use of a new and improved organic bonding agent for foundry structures which substantially overcomes the defects of the bonding agents employed in the art. The organic bonding agent of this invention was prepared by a heat treatment of the colored resin by-product of the refining of FF wood rosin, either alone, or blended with other pine wood resin which had been extracted from pine wood with aromatic hydrocarbons and which was substantially insoluble in petroleum hydrocarbons, in the presence of about 1% boric acid, based on the weight of the resin, with or without simultaneous air-blowing, or by a heat treatment and air-blowing, but without the addition of boric acid. The melting point of the resin was raised from about 185° F. (85° C.) to from about 194° F. (90° C.) to about 320° F. (160° C.). The resultant resin from the general treatment described above is specifically illustrated in the following examples, and, hereinafter in this specification, will be indicated as the "modified resin product." The modified resin product may be used in a concentration of from about 0.1% to about 10%, by weight of the total weight of the foundry structure, but preferably from about 0.5% to about 3%, to bond any foundry core or mold comminuted refractory material.

The method of preparing foundry structures accordant with the present invention comprises mixing the organic bonding agent with a comminuted refractory material and then mixing water therein. The cores or molds are then rammed from this mix and dried at an elevated temperature. More specifically, the modified resin product bonding agent of this invention

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may be incorporated with the body material of a foundry structure by grinding it to a solid powder and mulling the bonding agent and body material, or the binder may be dissolved in a suitable solvent or solvent mixture, such as alcohol, an aromatic hydrocarbon, a mixture of aromatic hydrocarbons or an alcohol-aromatic hydrocarbon mixture, and the solution mixed with the body material, while mulling, thus giving a uniformly treated body material. Additionally, the foundry structure incorporating the modified resin binder may be surface treated, in whole or in part, with a suitable solution or dispersion of the modified resin product followed by drying in air or in an oven, or by burning or torching. The solution or dispersion of the modified resin product may incorporate a finely-divided refractory material, such as graphite, plumbago, silica flour, etc., when desired for certain metal finishes.

Having now indicated in a general way the nature and purpose of the invention, there follows a more detailed description in which the following examples are given for the purpose of illustration.

EXAMPLE I

Three thousand parts of New Jersey No. 60 silica sand and 60 parts of a pulverized modified resin product of the colored resin by-product of the refining of FF wood rosin, melting point (drop) 243° F. (117° C.), prepared by heating the colored resin by-product of the refining of FF wood rosin with 1% of its weight of boric acid for three hours at 338° F. (170° C.) while agitating the mixture by blowing with carbon dioxide, were mixed together for three minutes in a muller. Two hundred ten parts of water was added, and mulling continued for an additional three minutes. Cores rammed from this mix were baked for one hour at 400° F. On cooling to atmospheric temperature, baked cores had the following physical properties:

Compression strength.....lbs. per sq. in. 193
Tensile strength.....do. 40
Transverse strength.....do. 9
Scratch hardness No.....50

For purposes of comparison cores were made in a similar manner, except for substituting B wood rosin for the modified resin product and were found to have the following properties:

Dry compression strength.....lbs. per sq. in. 155
Tensile strength.....do. 17
Transverse strength.....do. 8
Scratch hardness No.....45

EXAMPLE II

Three thousand parts of New Jersey No. 60 silica sand and 60 parts of a pulverized modified resin product of the colored resin by-product of the refining of FF wood rosin, melting point (drop) 221° F. (105° C.), which was prepared by air-blowing of the colored resin by-product of the refining of FF wood rosin for six hours at 338° F. (170° C.), were muller together for three minutes. Two hundred ten parts of water was then added, and mixing was continued for an additional three minutes. Cores rammed from this mix were baked for one hour at 400° F., following which they were removed from the oven and allowed to cool to atmospheric temperature.

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Resulting cores had the physical properties listed below:

Compression strength.....lbs. per sq. in. 210
Tensile strength.....do. 45
Transverse strength.....do. 10
Scratch hardness No.....50

EXAMPLE III

In order to illustrate the superior nature of the modified resin product of the colored resin by-product of the refining of FF wood rosin described in the first two examples as partial replacements of raw linseed oil, the mixes listed in Table 1 were prepared. Physical data obtained clearly show that these resins may be satisfactorily used to partially replace the more expensive drying oils, giving cores which bake faster and have somewhat greater strength.

TABLE 1

Use of modified resin products as partial replacements of raw linseed oil in foundry core mixes

Mix No.	1	2	3	4	5
New Jersey No. 60 Silica Sand					
Raw Linseed Oil.....parts..	3000	3000	3000	3000	3000
Modified Resin Product melting point (drop) 243° F. (117° C.) ¹	30	22.6	22.5	15	15
Modified Resin Product melting point (drop) 221° F. (105° C.) ²		7.5		15	
Water Added.....do.	145	145	145	145	145
Mixing Conditions.....	3 minutes dry—3 minutes oil—3 minutes water				
Moisture Determined.....percent..	4.0	4.0	4.0	4.0	4.2
Baking Time.....hours.	1½	1½	1½	1½	1½
Baking Temp.....°F.	425	425	425	425	425
Green Permeability No.	103	103	107	112	112
Green Compression Strength ³	0.6	0.4	0.4	0.5	0.4
Flowability.....percent..	92	90	91	90	91
Dry Compression Strength ³	357	400	470	463	391
Tensile Strength ³	78	91	105	96	87
Transverse Strength ³	20	22	25	20	19
Scratch Hardness No.	65	70	70	65	65
Dry Permeability No.	122	115	119	128	134

¹ Modified resin product prepared by heating the colored resin by-product of the refining of FF wood rosin with 1% of its weight of boric acid for three hours at about 338° F. (170° C.), agitating the mixture by blowing with carbon dioxide.

² Modified resin product prepared by air-blowing of the colored resin by-product of the refining of FF wood rosin for six hours at about 338° F. (170° C.).

³ Expressed as pounds per square inch.

EXAMPLE IV

Three thousand parts of New Jersey No. 60 silica sand and 60 parts of a pulverized modified resin product of the colored resin by-product of the refining of FF wood rosin, melting point (drop) 237° F. (114° C.), prepared by air-blowing the colored resin by-product of the refining of FF wood rosin and 1% of its weight of boric acid for 21 hours at a temperature of 334° F.—365° F. (168° C.—185° C.), were muller together for three minutes. Two hundred ten parts of water was then added and mulling continued an additional three minutes. Cores rammed from this mix were baked for one hour at 350° F., removed from the oven, and allowed to cool to atmospheric temperature. The cores had the following properties as a result of the modified resin product of the colored resin by-product of the refining of FF wood rosin binder contained therein:

Compression strength.....lbs. per sq. in. 270
Tensile strength.....do. 50
Transverse strength.....do. 9
Scratch Hardness No.....50

EXAMPLE V

Cores comprising reclaimed sand in conjunction

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with the modified resin product of this invention possess enhanced compression strength to such an extent that less of the binder may be used, thereby producing an economy, with still excellent casting properties. This is illustrated in the following example:

Fifteen hundred parts of New Jersey No. 60 silica sand, 1500 parts of a steel foundry reclaimed sand, and 60 parts of a pulverized modified resin product of the colored resin by-product of the refining of FF wood rosin, melting point (drop) 237° F. (114° C.), which had been prepared by air-blowing the colored resin by-product of the refining of FF wood rosin and 1% of its weight of boric acid for 21 hours at a temperature of 334° F.-365° F. (168° C.-185° C.), were mulled together for three minutes. Two hundred ten parts of water was then added and mixing continued for another three minutes. The mix was then emptied into a suitable container. Cores rammed from this mix were baked for one hour at 400° F., removed from the oven, and allowed to cool to atmospheric temperature. Resulting cores had the following physical properties:

Compression strength-----lbs. per sq. in--	628
Tensile strength-----do-----	102
Transverse strength-----do-----	21
Scratch Hardness No-----	72

EXAMPLE VI

The following is indicative of the exceptionally high dry compression and tensile strengths that are obtained when the modified resin of this invention is incorporated with reclaimed sand to make foundry cores and molds.

Three thousand parts of a steel foundry reclaimed sand and 60 parts of a pulverized modified resin product of the colored resin by-product of the refining of FF wood rosin, melting point (drop) 237° F. (114° C.), which had been prepared by air-blowing the colored resin by-product of the refining of FF wood rosin and 1% of its weight of boric acid for 21 hours at a temperature of 334° F.-365° F. (168° C.-185° C.), were mulled together for three minutes. Two hundred ten parts of water was added and mixing continued for another three minutes. The mix was then emptied into suitable containers. Cores rammed from this mix were baked for one hour at 400° F., removed from the oven, and allowed to cool to atmospheric temperature. Resulting cores had the following physical properties:

Compression strength-----lbs. per sq. in--	806
Tensile strength-----do-----	119
Transverse strength-----do-----	27
Scratch Hardness No-----	82

EXAMPLE VII

Three thousand parts of McConnellsville sand and 90 parts of a pulverized modified resin product of the colored resin byproduct of the refining of FF wood rosin, melting point (drop) 237° F. (114° C.), which had been prepared by air-blowing the colored resin by-product of the refining of FF wood rosin and 1% of its weight of boric acid for 21 hours at a temperature of 334° F.-365° F. (168° C.-185° C.), were mulled together for three minutes. One hundred ninety-five parts of water was added and mixing continued for an additional three minutes. The mix was then emptied into suitable containers. Cores rammed from this mix were baked for one hour at 400° F., removed from the oven, and cooled to atmos-

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pheric temperature. Physical data obtained on resulting cores are given below:

Compression strength-----lbs. per sq. in--	408
Tensile strength-----do-----	30
Transverse strength-----do-----	10
Scratch Hardness No-----	65

EXAMPLE VIII

Two thousand eight hundred fifty parts of New Jersey No. 60 silica sand, 150 parts of Western bentonite, and 30 parts of a pulverized modified resin product of the colored resin by-product of the refining of FF wood rosin, melting point (drop) 237° F. (114° C.), which had been prepared by air-blowing the colored resin by-product of the refining of FF wood rosin and 1% of its weight of boric acid for 21 hours at a temperature of 334° F.-365° F. (168° C.-185° C.), were mulled together for two minutes. One hundred thirty-eight parts of water was added and mixing continued for an additional five minutes. Mold specimens rammed from this mix were dried for two hours at 230° F., removed from the oven, and allowed to air-cool to atmospheric temperature. Physical data obtained on green and dried molds containing modified resin product of the colored resin by-product of the refining of FF wood rosin are given in Table 2. Data are also presented on molds bonded with bentonite alone, and with 1% cereal binder added, to illustrate the advantages derived from the addition of the modified resin product.

TABLE 2

Use of modified resin products of the colored resin by-product of the refining of FF wood rosin as a foundry mold binder

Mix No.-----	1	2	3
New Jersey No. 60 Silica Sand-----parts..	2850	2850	2850
Western Bentonite-----do-----	150	150	150
Cereal Binder-----do-----		30	
Modified Resin Product melting point (drop) 237° F. (114° C.) ¹ -----parts..			30
Water Added-----do-----	138	138	138
Mixing Conditions-----	2 minutes dry-- 5 minutes water.		
Moisture Determined-----per cent..	4.1	4.0	4.0
Drying Time-----hours..	2	2	2
Drying Temp.-----°F.	230	230	230
Green Permeability No.-----	102	98	89
Green Compression Strength ² -----	5.6	7.7	7.0
Deformation (in./in.)-----	0.018	0.031	0.018
Flowability-----per cent..	83	79	82
Mold Hardness No.-----	77	79	79
Dry Compression Strength ² -----	133	128	219
Dry Permeability No.-----	138	134	115

¹ Modified resin product prepared by air-blowing the colored resin by-product of the refining of FF wood rosin and 1% of its weight of boric acid for 21 hours at 168-185° C.

² Expressed as pounds per square inch.

EXAMPLE IX

Six thousand parts of New Jersey No. 60 silica sand and 120 parts of a pulverized modified resin product of the colored resin by-product of the refining of FF wood rosin, which had been modified by air-blowing the colored resin by-product of the refining of FF wood rosin to produce pale grades of wood rosin, for 20 hours at 338° F., were mulled together for three minutes. Four hundred twenty parts of water was then added and mixing continued for an additional three minutes. Cores rammed from this mix were baked for one hour at 500° F., removed from the oven, and allowed to cool to atmospheric temperature.

This same procedure was repeated using as a binder: (1) A modified resin product of a one to one resin blend of pine wood resin substantially insoluble in petroleum hydrocarbons and the col-

ored resin by-product of the refining of FF wood rosin to produce pale grades of wood rosin, which had been modified by air-blowing the resin blend for 6¼ hours at 356° F.; and (2) a modified resin product of a one to one resin blend of pine wood resin substantially insoluble in petroleum hydrocarbons and the colored resin by-product of the refining of FF wood rosin to produce pale grades of wood rosin, which had been modified by treating the resin blend with 0.5% boric acid by weight followed by air-blowing for 1½ hours at 356° F.

Physical data for the prepared cores are given in Table 3 below and demonstrate that the addition of substantially petroleum hydrocarbon-insoluble pine wood resin to the colored resin by-product of the refining of FF wood rosin before modification by a heat treatment with simultaneous air oxidation with and without boric acid, improves the properties of foundry cores prepared therewith.

TABLE 3

Use of modified resin products as foundry core binders

Mix. No.	1	2	3
New Jersey No. 60 Silica Sand..... parts.	6000	6000	6000
Modified Resin Product ¹	120		
Modified Resin Product ²		120	
Modified Resin Product ³			120
Water Added..... parts	420	420	420
Mixing Conditions.....	3 minutes dry—3 minutes wet.		
Moisture Determined..... per cent.	6.1	6.1	6.1
Baking Time..... hours	1	1	1
Baking Temp..... °F.	500	500	500
Green Permeability No.....	83	72	76
Green Compression Strength ⁴	1.3	1.2	1.2
Flowability.....	88	84	84
Dry Compression Strength ⁴ per cent.	227	322	273
Tensile Strength ⁴	34	58	46
Transverse Strength ⁴	8	11	10
Hardness No. (Flow).....	35	40	40
Hardness No. (Scratch).....	50	60	60
Dry Permeability No.....	134	122	126

¹ Prepared by air-blowing the colored resin by-product of the refining of FF wood rosin to pale grades of wood rosin, for 20 hours at 338° F.

² Prepared by air-blowing a 1 to 1 resin blend of substantially petroleum hydrocarbon-insoluble pine wood resin and the colored resin by-product of the refining of FF wood rosin to pale grades of wood rosin, for 6¼ hours at 356° F.

³ Prepared by air-blowing a 1 to 1 resin blend of substantially petroleum hydrocarbon-insoluble pine wood resin and the colored resin by-product of the refining of FF wood rosin to pale grades of wood rosin, to which 0.5% boric acid had been added, for 1½ hours at 356° F.

⁴ Expressed as pounds per square inch.

EXAMPLE X

Two foundry core and mold sprays were prepared as follows:

RESIN SPRAY OF MODIFIED RESIN PRODUCT

	Parts
Modified resin product ¹	150
2B alcohol.....	425
Solvesso No. 1 ²	425

¹ Prepared by air-blowing the colored resin by-product of the refining of FF wood rosin for 20 hours at 338° F.

² Petroleum hydrocarbon product high in aromatics.

The pulverized modified resin product was slowly added to the solvent mixture, with stirring, and stirring continued until complete solution of the resin occurred. Graphite, as a refractory material, was added to a portion of the above-prepared spray in the following proportions to produce a resin spray containing a refractory:

MODIFIED RESIN PRODUCT SPRAY CONTAINING A REFRACTORY

	Parts
Modified resin product solution.....	400
Graphite.....	100

The following core mix was then prepared:

New Jersey No. 60 silica sand..... parts.	3000
Cereal binder..... do.	30
Water added..... do.	210
Moisture determined..... per cent.	6.1

Cores rammed from this mix were baked for one hour at 400° F., removed from the oven, and allowed to cool to room temperature.

The above cores were sprayed with each of the prepared spray compositions, and allowed to dry for one-half hour at 230° F.

Hardness tests carried out on the resulting cores gave the following results:

Cores Sprayed With—	Scratch Hardness No.
Resin Spray Without Refractory.....	80
Resin Spray With Refractory.....	80
Unsprayed Core.....	60

It was also noted that the unsprayed cores had rather soft surfaces. Edges were easily rubbed off on handling. The sprayed cores had hard surfaces which were not readily damaged by handling. Graphite was firmly held on the core surfaces by the modified resin product, and could not be rubbed off easily.

This demonstrates the advantages to be gained by using the modified resin product of this invention in solution, with and without a refractory added, as a foundry core and mold spray.

EXAMPLE XI

A modified resin product was prepared by air-blowing the colored resin by-product of the refining of FF wood rosin mixed with 1% of its weight of boric acid for 21 hours at 334° F.—365° F. (168° C.—185° C.). The modified resin product was dissolved in a solvent to form a liquid binder, as follows:

RESIN BINDER SOLUTION

	Parts
Modified resin product.....	250
Solvesso No. 2 ¹	250

¹ Petroleum hydrocarbon product high in aromatics.

The resin was heated in a suitable vessel to a top temperature of 375° F., following which the Solvesso was added, with stirring, and the mixture stirred until complete solution was obtained.

The following core mix was then prepared:

Three thousand parts of New Jersey No. 60 silica sand and 90 parts of the above resin binder solution were mulled together for three minutes. One hundred twenty parts of water were added and mixing continued for another three minutes.

Cores rammed from this mix were baked for one hour at 400° F., removed from the oven, and allowed to cool to room temperature. Resulting cores had the following physical properties:

Dry compression strength..... lbs. per sq. in.	131
Tensile strength..... do.	27
Transverse strength..... do.	8
Scratch hardness No.....	45

The organic bonding agent of this invention is a modified resinous product of a resin, which is itself the residue of the selective solvent treatment of FF wood rosin to produce pale grades of wood rosin, either alone, or blended with other pine wood resin which is extractable from pine wood with aromatic hydrocarbons and which is

substantially insoluble in petroleum hydrocarbons.

The said resin which is itself the residue of the selective solvent treatment of FF wood rosin to produce pale grades of wood rosin, is well known in the art as the product of the Kaiser and Hancock U. S. Patent 1,715,088 and has, as is well known from the Langmeier U. S. Patent 2,242,529, substantially the following approximate analysis:

Acid number-----	105-140
Saponification number-----	150-170
Melting point (Hercules drop method) -----°F. ¹	176-239
Unsaponifiable matter-----per cent--	10-20
Gasoline insoluble-----do-----	30-80
Petroleum ether insoluble-----do-----	30-80
¹ 80° C.-115° C.	

The pine wood resin which is extractable with aromatic hydrocarbons and which is substantially insoluble in petroleum hydrocarbons is the well known petroleum hydrocarbon-insoluble pine wood resin extract of Hall, U. S. 2,193,026, and has substantially the following characteristics: substantial insolubility in petroleum hydrocarbons, substantially complete solubility in alcohol, a methoxy content of from about 3% to about 7%, an acid number of from about 80 to about 110, a melting point by the Hercules drop method of from about 95° C. to about 125° C., and a non-carboxylic hydroxyl content of from about 5% to about 9%.

Thus, the resin, or mixture of resins, to be modified, may be any portion or substantially all of that dark-colored fraction of pine wood resin which can be extracted from the wood with aromatic hydrocarbons and which is characterized by a petroleum hydrocarbon-insolubility of from about 30% to about 95%, the particular composition and characteristics of any one portion being determined by the conditions of the selective solvent fractionation of the pine wood resin in separating out the pale grades of wood rosin, or other methods employed in refining pine wood resins.

The modified resin product of this dark-colored fraction, or any sub-fraction or combination of sub-fractions thereof, of pine wood resin which fraction is extractable from pine wood with aromatic hydrocarbons and which is characterized by containing from about 30% to about 95% of material which is insoluble in petroleum hydrocarbons, such as gasoline and petroleum ether, is the resin prepared by treatment of the said fraction of pine wood resin with boric acid at suitable temperatures, with or without simultaneous air oxidation or by air oxidation alone at suitable temperatures. The resulting product should have a melting point of from about 194° F. (90° C.) to about 320° F. (160° C.), and preferably above about 230° F. (110° C.). It can be readily ground, stored, and shipped without danger of reversion.

The sand used to form the foundry structure is the ordinary foundry sand such as washed and dried silica sand, crude silica sand, lake sand, bank sand, loam, natural bonded molding sand, reclaimed heap sand, etc. Additionally, for use in molds, any clay or clay-like material such as fire clay, ball clay, china clay, fuller's earth, bentonite, etc., is applicable.

Thus, this invention relates to the use of a modified resin product of the dark-colored fraction of pine wood resin which is extractable from pine wood with aromatic hydrocarbons and which contains from about 30% to about 95% petroleum hydrocarbon-insoluble material, with foundry

sands used either in making foundry cores or molds, the modified resin product being incorporated in foundry core and mold mixes either by mixing in the pulverized form or applying in the form of a spray of a solution or dispersion, or being applied to the surface of formed foundry structures as a solution in a solvent, or mixture of solvents, with or without an incorporated refractory, or in the form of a dispersion or as a paste.

The advantages of the present invention are that the modified resin: (1) may be readily mixed with reclaimed foundry sand, and since less binder is usually needed for rebonding, considerable savings result in sand and binder costs; (2) may be mixed with sands high in clay, as compared to liquid binders, to give strong hard cores; (3) may be baked faster than many prior art binders thus speeding production; (4) gives cores and molds which exhibit improved resistance to moisture absorption; (5) gives cores and/or molds highly resistant to the action of molten metal and yet burn out readily as to permit easy shakeout of core and molding sand; and (6) the pulverized resin does not undergo reversion to one substantially uniform solid mass, upon standing.

The green permeability number and dry permeability number given in the tables of the examples of the specification represent the number of cubic centimeters of gas passed per minute by a core specimen 1 cc. in volume such that there is a vacuum on one side of the cube and a gas pressure of 1 g./cm.² on the opposite side. The permeability was determined using a standard core permeability tube manufactured by the Harry W. Dietert Company of Detroit, Michigan.

The scratch hardness and plow hardness numbers are determined using a core hardness tester manufactured by the Harry W. Dietert Company of Detroit, Michigan. In the case of scratch hardness, the instrument is fitted with a diamond cone point. In the case of plow hardness, the instrument is fitted with a metal plow. The degree of hardness is designated by the depth of scratch produced by the diamond cone point or the plow. The plow or point is spring loaded so that when a static load of 1100 grams is applied, the plow or cone point protrudes 0.100 inch through the plate. A load of 2000 grams will cause the plow or cone point to become flush with the surface of the plate. The position of the plow or cone point in reference to the surface of the plate is indicated by a dial indicator reading in increments of 0.001 inch. When the plow or cone point is flush with the surface of the plate, the indicator reads 100 and when it protrudes 0.100 inch beyond the plate, the indicator reads 0. Thus, the readings are purely relative, a high degree of hardness being indicated by a large number, maximum hardness being indicated by 100. In general, the scratch hardness number for a given core is slightly higher than the plow hardness number.

What I claim and desire to protect by Letters Patent is:

1. A foundry core or mold comprising a comminuted refractory material and a binder consisting of a resinous material having a drop melting point of about 90° to about 160° C. and obtained by the simultaneous heat treatment and air oxidation, in the presence of boric acid, of a material of the group consisting of (1) the residue from the selective solvent refining of FF wood rosin, said residue being characterized by an acid number of 105 to 140, a saponification number of 150 to 170, a drop melting point of

80° to 115° C., an unsaponifiable matter content of 10 to 20%, a gasoline insolubility of 30 to 80%, and a petroleum ether insolubility of 30 to 80%; and (2) the mixture of said residue from the selective solvent refining of FF wood rosin and the substantially petroleum hydrocarbon-insoluble pine wood resin characterized by an acid number of 80 to 110, a drop melting point of 95° to 125° C., a methoxy content of 3 to 7%, and a noncarboxylic hydroxyl content of 5 to 9%.

2. A foundry core or mold comprising a comminuted refractory material and from about 0.1 to about 10% based on the weight of the refractory material of a binder consisting of a resinous material having a drop melting point of about 90° to about 160° C. and obtained by the simultaneous heat treatment and air oxidation, in the presence of boric acid, of a material of the group consisting of (1) the residue from the selective solvent refining of FF wood rosin, said residue being characterized by an acid number of 105 to 140, a saponification number of 150 to 170, a drop melting point of 80° to 115° C., an unsaponifiable matter content of 10 to 20%, a gasoline insolubility of 30 to 80%, and a petroleum ether insolubility of 30 to 80%; and (2) the mixture of said residue from the selective solvent refining of FF wood rosin and the substantially petroleum hydrocarbon-insoluble pine wood resin characterized by an acid number of 80 to 110, a drop melting point of 95° to 125° C., a methoxy content of 3 to 7%, and a noncarboxylic hydroxyl content of 5 to 9%.

3. A foundry core or mold comprising a comminuted refractory material and from about 0.5 to about 3% based on the weight of the refractory material of a binder consisting of a resinous material having a drop melting point of about 90° to about 160° C. and obtained by the simultaneous heat treatment and air oxidation, in the presence of boric acid, of a material of the group consisting of (1) the residue from the selective solvent refining of FF wood rosin, said residue being characterized by an acid number of 105 to 140, a saponification number of 150 to 170, a drop melting point of 80° to 115° C., an unsaponifiable matter content of 10 to 20%, a gasoline insolubility of 30 to 80%, and a petroleum ether insolubility of 30 to 80%; and (2) the mixture of said residue from the selective solvent refining of FF wood rosin and the substantially petroleum hydrocarbon-insoluble pine wood resin characterized by an acid number of 80 to 110, a drop melting point of 95° to 125° C., a methoxy content of 3 to 7%, and a noncarboxylic hydroxyl content of 5 to 9%.

4. A foundry core or mold comprising sand, a clay-like material, and a binder consisting of a resinous material having a drop melting point of about 90° to about 160° C. and obtained by the simultaneous heat treatment and air oxidation,

in the presence of boric acid, of a material of the group consisting of (1) the residue from the selective solvent refining of FF wood rosin, said residue being characterized by an acid number of 105 to 140, a saponification number of 150 to 170, a drop melting point of 80° to 115° C., an unsaponifiable matter content of 10 to 20%, a gasoline insolubility of 30 to 80%, and a petroleum ether insolubility of 30 to 80%; and (2) the mixture of said residue from the selective solvent refining of FF wood rosin and the substantially petroleum hydrocarbon-insoluble pine wood resin characterized by an acid number of 80 to 110, a drop melting point of 95° to 125° C., a methoxy content of 3 to 7%, and a noncarboxylic hydroxyl content of 5 to 9%.

5. The method of making a foundry core or mold comprising mixing a comminuted refractory material, a binder consisting of a resinous material having a drop melting point of about 90° to about 160° C. and obtained by the simultaneous heat treatment and air oxidation, in the presence of boric acid, of a material of the group consisting of (1) the residue from the selective solvent refining of FF wood rosin, said residue being characterized by an acid number of 105 to 140, a saponification number of 150 to 170, a drop melting point of 80° to 115° C., an unsaponifiable matter content of 10 to 20%, a gasoline insolubility of 30 to 80%, and a petroleum ether insolubility of 30 to 80%; and (2) the mixture of said residue from the selective solvent refining of FF wood rosin and the substantially petroleum hydrocarbon-insoluble pine wood resin characterized by an acid number of 80 to 110, a drop melting point of 95° to 125° C., a methoxy content of 3 to 7%, and a noncarboxylic hydroxyl content of 5 to 9%, sufficient water to render the mass workable, ramming the mix into a foundry structure pattern, and baking at a temperature from about 250° to about 650° F.

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