

UNITED STATES PATENT OFFICE

2,313,672

COATING SAND MOLD SURFACES

Harold K. Salzberg and Walter B. Kinney, Bain-
bridge, N. Y., assignors to The Borden Com-
pany, New York, N. Y., a corporation of New
Jersey

No Drawing. Application August 6, 1941,
Serial No. 405,718

7 Claims. (Cl. 22—189)

Metal castings prepared by pouring molten metal into sand molds are in large measure dependent for their properties and quality on the character of the mold and core surfaces against which the molten metal flows and sets. The smoothness of the sand surfaces, their ability to conduct heat and gases and their reaction to the heat of the metal are factors which have an important bearing on the quality of the castings.

Foundry sand practice properly embraces the treatment of molds and cores with coatings to improve casting quality. The general methods of special treatment of mold and core surfaces include (1) preparation of a special facing sand, (2) coating the sand surfaces with a prepared suspension of refractory material, (3) dusting on finely divided refractory powders, and (4) spraying the surfaces with solutions of adhesive materials.

The preparation of a special facing sand involves the mixing of a fine clean sand with water and binders which provide the necessary strength and working properties or moldability to the sand. This sand is mixed separately from the main bulk of the sand, and often in mixing equipment set aside for the purpose. This sand is applied to the pattern or core box first, against which it forms a thin layer, which becomes the face of the mold or core and against which the molten metal directly contacts, if no coating is subsequently applied to the facing. Facing sand is carefully prepared and closely controlled to provide the best possible mold and core surfaces.

Instead of a specially prepared facing sand, the mold or core surface may be one of a refractory material applied as a coating to an ordinary sand surface, or this coating may be applied to a special facing sand, thus combining the advantages of both methods of providing a satisfactory sand surface. These coatings in the foundry art are suspensions of fine silica, mica, graphite, zircon, clays or other refractory material, applied in liquid form by brushing, spraying or dipping the molds and cores. Upon drying they provide a smooth and heat resistant coating which largely prevents the burning of sand onto metal.

On occasion the dispersing of the refractory material into liquid form is dispensed with and dry powdered refractory material is dusted onto the damp sand surfaces. Thus silica flour or graphite might be dusted onto parts of molds or cores which require some protection because of severe action of the flowing metal, as for instance near the gate or point of entry of the

molten metal to the mold, or around bends in the design which are subjected to severe erosion as the mold fills. Though less commonly employed, this is one method of improving core and mold surfaces.

Another method directed at the same objective involves coating, usually by spraying, of the sand surfaces with solutions of materials which are adhesive in nature, or become so on drying, and thus act as auxiliary or additional binders for the face of the sand. The application of a spray imparts extra strength and a "crust" or "skin" to the sand on drying. Usually water soluble materials are employed, such as molasses, sulfite waste liquor, dextrin, sodium silicate, etc., but sometimes oils are applied or sprayed on. These same solutions at times serve as the medium for suspending finely divided refractory material to prepare coatings of the second class described above.

The demands of the production schedule or of the casting design will dictate which of the methods described is to be used in any one foundry for any certain job, but they all have the common purpose of improving the quality of the casting.

The facing sand, binder, coating, or spray must meet certain demands of performance to be acceptable in the foundry art. One important requirement being that of strengthening the sand surface, the material may serve as binder for the sand grains, that is, may set or dry to a bond "cementing" the sand grains. All or a portion of such binder must be combustible or destructible by heat, particularly if applied to dry sand cores which are to be positioned internally in the mold and around which the metal is to flow and set. In general, a readily heat destructible bond is sought so that the strength of the sand mold or core is rapidly lost as the newly poured casting cools and shrinks. A three-fold advantage results from combustion or destruction of the binder and ready collapsibility of the sand, namely (1) elimination of barriers to the changing dimensions of the casting as it cools, (2) transformation of the hard and strong sand parts into free flowing sand easily removed from the casting, and (3) destruction of the temporary seal which the coating or spray provides to the sand surfaces, thus permitting egress of gases from the mold.

There are other more obvious requirements of a good facing material or coating. If the material is in the liquid form it should preferably be of high stability, not changing in storage or

handling, as by separating or fermenting. In many types of foundry sand work the production schedule will not permit of the application of any material not conveniently applied. A coating or spray must therefore be of such a nature that it can be applied rapidly and uniformly to either wet or dry sand surfaces without damaging, tearing or rolling up the sand. The material must preferably penetrate quickly into the sand to prevent running and to insure uniformity of strength, hardness and thickness over the entire surface of the mold or core. Strength is developed by drying or hardening, and this drying or hardening must take place within a reasonable period of time.

A further requirement of a good facing or coating material is that, when dry, it should withstand moisture of the air; that is, should resist the harmful effect of moisture of the atmosphere of either the foundry or the closed mold. Oils are preferred for dry sand work because the oil coatings withstand damp air. The compositions utilized in the present invention also withstand the effects of moisture and provide moisture-resistant molds and cores.

This invention is based upon the discovery of new combinations of materials for the purpose of improving sand mold and core surfaces, in the development of which the necessary qualities discussed above have been provided, and which, in addition, possess advantages over those materials heretofore used for the purpose. Two primary types of ingredients comprise the finished material used in the invention, (1) a condensate in the water-soluble or solvent-soluble stage of a thermosetting synthetic resin and (2) a drying oil, drying oil-natural resin mixture, or drying oil alkyd resin or blends of these. As herein-after described either or both of these main ingredients may be modified and additions made to the mixture of them.

The dry mold or core surface bonded or coated with a mixture of thermosetting synthetic resin condensate and drying oil or drying oil compound differs from cores and molds bonded or coated with straight core oil in being highly collapsible by heat and therefore yielding readily to the pressure exerted by the cooling and shrinking casting. This feature of high collapsibility contributes to casting quality in reducing the amount of burned-on sand and the cracks which might form in the sections of the casting as it shrinks. High collapsibility also means easy removal of burned sand from the casting. The feature of high collapsibility of core or mold is especially advantageous in the pouring of lead, aluminum or magnesium alloy castings where the metal heat is relatively low; but is also of advantage in the pouring of other metals where shrinkage percentages are high as with certain steels and where the design of the casting is such that shrinkage cracks are likely to occur because of unequal shrinkage in different parts of the casting.

To illustrate the rapid response of thermosetting synthetic resin to high temperature, cores in the form of test bars were prepared and sprayed with an urea-formaldehyde resin condensate in the water-soluble stage and then subjected to a temperature of 600° F. for increasing periods of time. This temperature of 600° F. is substantially above that of core oven temperatures in practice and lies within a temperature range prevailing a short distance back from the actual sand surfaces of the mold or core. There-

fore the effect of temperature on strength of core shown in the table below can be taken as indicative of rate of collapse of sand as it acquires heat from the metal immediately following pouring of the mold. The comparative performance under heat of this resin and a widely used core oil is shown.

Time at 600° F.	Resin-sprayed core	Oil-sprayed core
15 min	14.07	No strength
45 min	4.67	19.67
75 min	No strength	17.93

Values are lbs. per sq. in. transverse strength.

In this test the urea resin solution was of condensation corresponding to the attainment of a solution containing 62 per cent resin solids, and was prepared by reacting under heat two mols of formaldehyde with one mol of urea, followed by condensation to the aforesaid solution of 62 per cent resin solids. Both the resin and the oil types of spray were applied in such amount that each increased the weight of the dry core by the same amount.

The breakdown of a thermosetting resin may be so rapid that it is often not practical to bake cores, sprayed with such type of resin alone. The purpose of admixture of drying oil or drying oil alkyd resin with the synthetic resin is to provide protection to the latter while the core is drying or baking, without destroying the advantage of rapid collapsibility when the metal is poured and the sand subjected to the temperature of the molten metal. Numerous practical foundry trials have proved that in these combinations of materials the proper degrees of heat resistance depending upon the demands of the metal and the casting design can be provided.

When sprayed onto the sand surfaces of cores and molds, a combination of ingredients according to this invention penetrates rapidly but not deeply. This behavior constitutes a second important advantageous difference in the performance of a spray according to the present invention over oils of the class known as core oils. Measurements have been made of the depth of penetration of a spray according to the present invention and of the usual core oils in a commonly used core sand. In one test the two types of spray were applied by spray gun to green sand core test bars in amounts so that equal increase in weight of the sprayed core on the solids basis resulted. Upon visual examination the depth of penetration was found to have been as follows:

Millimeters

Synthetic resin-oil emulsion	2
Core oil A	9
Core oil B	9

Shallow penetration results in concentration of the spray material at or near the surface of the core or mold thus providing a two-fold advantage, viz. (1) increased strength and hardness at the surface and (2) shell structure to the core or mold. The increased strength and hardness at the surface of the sand is added protection against breakage in handling, and secondly, increased surface hardness promotes chilling of the hot metal. Shell structure in cores in varying degree depending upon design of casting is desirable, for a soft-centered core is more readily collapsible and more friable, thus more readily removed from the casting, than a solid core.

A third characteristic of a spray according to the present invention, and which present core oils do not possess, is its ability to dry in the air at room temperature. Green cores, when sprayed according to the present invention, acquire a "skin" within a few minutes by virtue of the rapid drying of the spray coating. This "skin" possesses strength and serves as protection against dropping or distortion while the sand is in the green stage. Such a core or mold stands up better under the jarring and vibration incident to conveying to the core oven and therefore provides cores of the more intricate designs with dimensions within minimum tolerances.

A fourth characteristic of a spray according to the present invention, and which core oils do not possess, is its strength in hot cores. The synthetic resin ingredient is not a thermoplastic material and therefore is not soft at the temperatures usually prevailing in the core oven. On the contrary, the sprayed cores are substantially as hard when as hot as core oven temperatures of about 400° F. as at room temperature. Therefore the hardness of surface of the core is maintained all through the oven cycle and during handling of the hot cores.

The thermosetting synthetic resin ingredient may be of the urea-aldehyde type or of the phenol-aldehyde type. For very rapid breakdown under heat the former type of resin is preferred. As commercial thermosetting resins of this type the following are available and are suitable for use in carrying out the practice of this invention: (1) urea-aldehyde products condensed to the stage where they are still soluble in water and in the preparation of which one mol of urea may be reacted with from one to three mols of aldehyde; (2) urea-aldehyde resins as a class generally referred to as "solvent-soluble", condensed in the presence of alcohols, providing a final resin which is miscible with organic solvents; (3) amine- and amide-aldehyde thermosetting resins, exemplified by (a) melamine-formaldehyde resins and (b) sulfonamide-formaldehyde resins; (4) phenol-aldehyde products condensed to the stage where they are still soluble in water and in the preparation of which one mol of phenol may be reacted with from one to three mols of formaldehyde; (5) resins of the above classes modified by the addition of protein material, e. g. casein, before condensation of the ingredients is effected; (6) resins of the above classes modified by the addition of seed meal flour, e. g., peanut meal and soybean meal, or of chitin or hydrolyzed chitin material, before condensation of the ingredients is effected.

The degree of condensation of the thermosetting resin need not be narrowly defined to be useful for the purpose of the present invention; however, it is required that the resin be at a stage of condensation where it is readily soluble in either water or organic solvents. In the case of the urea-formaldehyde resin this stage can be the "arrested" monomethylol or diemethylol urea stage in which case these water-soluble intermediates of definite simple molecular structure are depended upon to resinify under heat of the core baking process, or the resin may be at the higher intermediate condensed stage characterized by existing in solution in water or organic solvent and capable of maintaining this liquid condition for several months at room temperature. The phenolic types of resin, to be useful in this invention, are condensed only to an initial stage, still soluble, and known generally accord-

ing to the Baekeland designation as phase A. For practical purposes these resins also must be in solution at such a stage of condensation that the solution remains fluid for a period of several months. Resins condensed to this stage where the solution has a "life" of from three to six months at room temperature represent the preferred stage of condensation.

Foundry sprays of this invention are conveniently made in concentration of about 50% solids in water. To prepare for spraying, a dispersion of this concentration is best thinned with water to spraying consistency. Because of this requirement it is preferable to use a thermosetting resin which will not separate on strong dilution with water. This is provided among the types of resin listed above, and particularly a resin of type (5) such as casein stabilized urea-formaldehyde condensate.

Regular commercial solutions of formaldehyde resin ordinarily contain at the time of use a certain small percentage of free formaldehyde. If such a product would be used as a spray in an open room continual exposure to the formaldehyde fumes would be undesirable. Therefore treatment of the thermosetting resin ingredient to fix the free formaldehyde is resorted to in the manufacture of the spray used in the present invention. For this purpose urea has been found satisfactory.

The drying oil ingredient may be a natural drying oil, such as linseed or China-wood oil, or a synthetic resin of the alkyd type embodying drying oil as a reactant and possessing drying properties. The drying oil may be modified by the inclusion of a natural varnish resin, as for example rosin, ester gum, dammars, kauri or manilla fossil resins, or by admixture with synthetic resins, such as resins of the Bakelite type, or by blending with resins of petroleum origin, commonly known as cumar resins as a class. These additions to the drying oil all have the purpose of hardening the film. A combination of natural drying oil and a drying oil alkyd resin, as a mechanical mixture, may be used, thus reducing the cost of the material from what it would be in using straight drying oil alkyd resin. The choice of a drying oil, drying oil plus resin or a drying oil alkyd resin rests primarily upon the air-drying or air setting properties desired of the material in use. Fast drying drying oil alkyd resins are of special advantage where a quick air-set to the sand surfaces is desirable. To speed the drying of the coating or spray in service the usual catalytic oil driers, commonly known as "paint driers," are added in amounts of from 0.5 to 2% of the weight of drying oil or drying oil alkyd resin. These driers may be the fatty, naphthenic or resin acid salts of lead, cobalt and manganese, used in combination.

The drying oil alkyd resins, referred to above as suitable for the purposes of the present invention, comprise those resins classified as drying oil modified as "oxidizing" alkyds. They are solvent-soluble complex combinations of polybasic acids, glycerol and unsaturated fatty acids or natural resin acids and they are soluble in toluol, xylol and mineral spirits. The drying oil alkyd resins commercially available to the paint and varnish trade have been condensed to the stage which permits films of them to dry hard in 2 to 3 hours at baking temperature of 200-300° F. Exposed to the usual temperatures prevailing in the core oven, this class of resin therefore dries well within the usual baking periods.

The method of mixing drying oil or a drying oil alkyd resin with a water solution of the thermosetting synthetic resin is to first emulsify the drying oil or drying oil alkyd resin. As a fine dispersion in water, stabilized with an emulsifying agent, these materials are homogeneously blended with the thermosetting synthetic resin to form mixtures which do not separate and which are dilutable with water to provide satisfactory coating and spraying consistencies.

The emulsifying agents which may be employed include the commonly used materials capable of dispersing oils or drying oil alkyd resins in water, such as alkali soaps, amine soaps, alkali caseinates, alkali resinsates, bentonite, gums, proteinaceous materials, etc. The exact nature of the emulsifying agent is of consequence only in providing a fine oil-in-water type dispersion of good stability. As an illustration of the desired fineness of dispersed phase and stability of emulsion, if the particle size distribution falls within the range of one micron to ten microns and the emulsion of 50% concentration in water maintains its homogeneity and viscosity over a period of at least one month, the emulsion ingredient of the spray is considered satisfactory.

Examples of emulsions generally suitable for use in preparing the sprays for molds and cores for any type of cast metal are:

Emulsion A.—20 lbs. of acid casein is soaked in 200 lbs. of water and dissolved by heating in the presence of 6 oz. of magnesium hydrate and 2.5 lbs. of 26° ammonia. While the casein solution is still hot 230 lbs. of drying oil alkyd resin, warmed to fluidity if necessary, is mixed in and one per cent each of cobalt naphthenate liquid and lead naphthenate liquid, on the weight of the drying oil alkyd resin, added. The mixture is stirred and brought warm to the colloid mill. The dispersed phase, after passage through the colloid mill, will have a particle size distribution in the range of one to ten microns.

Emulsion B.—To a casein solution prepared as in making Emulsion A are added 230 lbs. of a mixture of 4 parts of linseed oil, 4 parts of ester gum and 1 part of VMP naphtha, 4.5 lbs. of linseed fatty acids and 1.8 lbs. of 26° ammonia. After thorough mixing, the warm liquid is passed through the colloid mill. The dispersed phase will have a particle size distribution in the range of less than one micron and up to two or three microns.

Emulsion C.—10 lbs. of linseed fatty acids (or the equivalent in other liquid fatty acids of high molecular weight) is stirred into 200 lbs. of warm water containing 4 lbs. of 26° ammonia. Keeping this soap solution warm, 230 lbs. of warm drying oil alkyd resin and one per cent each of cobalt naphthenate liquid and lead naphthenate liquid are stirred in. After passing through the colloid mill, the particle size distribution of the dispersed drying oil alkyd resin will lie in the range of less than one micron up to two or three microns. In this example the ammonia may be replaced by from one to three lbs. of commercial triethanolamine.

Emulsions B and C are more finely dispersed than Emulsion A and therefore are more suitable when used in making sprays for coating molds and cores made of the finer sands, because the more finely dispersed emulsions penetrate such sands more readily. When the sand is coarse such attention need not be given to fineness of dispersion. The use of Emulsions A and B in the spraying composition results in films which are

more resistant to moisture than films resulting from the use of Emulsion C; and this is a factor to be considered where dried cores are stored before use or where they are held for a time in a closed green sand mold before pouring.

To provide the highest possible degree of dispersion, the emulsion mixture is best run through a colloid mill or through an homogenizer. Another means of improving fineness of dispersed phase has been discovered in the thinning of the drying oils or drying oil alkyd resins with non-aqueous solvents. Lowering the viscosity of this ingredient results in finer dispersions and therefore we preferably reduce the viscosity of the drying oil or drying oil alkyd resin with mineral spirits, toluene or other solvent before emulsifying.

An alternative type of spray falling within the classification subject of this invention is the non-aqueous type. These compositions will be prepared by simply dissolving the drying oil or drying oil alkyd ingredient in the solvent-soluble type of resin condensate, thus providing mixtures which are now classified commercially as resin-modified baking enamel vehicles, compatible with the usual paint and varnish solvents. An advantage of this type of composition lies in the simplified manufacture of the mixture, the emulsifying step being eliminated. However, it is to be expected that the commercial use of such modifications will be limited because of (1) inflammability of the volatile solvents which will vaporize into the atmosphere of the foundry and (2) increased cost.

The liquid spray used in our invention thus preferably comprises primarily a mixture of water-soluble synthetic thermosetting resin condensate with a stable aqueous emulsion of a drying oil or a drying oil alkyd resin of suitably fine dispersion, or a mixture of a solvent-soluble synthetic thermosetting resin condensate with the unemulsified drying oil or drying oil alkyd resin. Additions may be made to these base mixtures to further enhance their performance. Included in such additions are (1) wetting agents to promote rapid penetration, (2) defoaming materials and (3) water-soluble dyes to impart color.

As an example of a suitable combination of water-soluble synthetic thermosetting resin condensate and drying oil alkyd emulsion for our purpose, we cite the following: A casein-modified urea-formaldehyde resin condensate is prepared by reacting one mol of urea with two mols of formaldehyde and 25 per cent of acid casein on the weight of urea by mixing dry urea and dried casein with aqueous formaldehyde under heat, then condensing to a total solids content of 40 per cent. 430 pounds of the resulting liquid is allowed to stand overnight with 20 pounds of solid urea. To the urea resin so treated is added 450 lbs. of Emulsion A described above. After mixing, the following are added in order: 10 lbs. of ammonia, 2 lbs. 10 ozs. of soda ash dissolved in 20 lbs. of water, 1 lb. of nigrosin dye dissolved in 30 lbs. of water and 2 lbs. of tributyl phosphate. The finished product will contain approximately 46% solids and have an initial reaction of between 7.5 and 7.8 in pH.

As an example of a non-aqueous spray we cite the following: Butanol-modified urea resin condensate, made by reacting formaldehyde with urea in the presence of butanol, followed by distilling off the water (as described in U. S. Patent 2,227,223 to Hodgins and Hovey) is diluted with mineral spirits to give a solution of 50 per cent

resin solids. 120 pounds of this solution is mixed with 60 pounds of drying oil alkyd resin, dissolved in 60 pounds of solvent naphtha. The resulting mixture of 50 per cent total resin solids is a clear liquid of good stability, of brushing consistency, and dilutable with mineral spirits or solvent naphtha to the lower concentrations of 10 per cent to 25 per cent solids ordinarily applied by the spraying method.

For purposes of describing the coating material used in the present invention, we have discussed its use as a spray. The manner of its application is not limited, however, to spraying. Occasionally the core or mold or part thereof may best be treated by brushing or swabbing on the liquid, and where particularly heavy coatings are desired this may be done with the concentrated fluid, dispensing with dilution. Although the full advantages of its properties are evident when cores are treated before baking or drying, the application may be made to cores after baking, either while they are still hot or after they have cooled. In the latter procedure a short secondary drying of the coated core will be necessary.

The application of the fluid mixtures used in the present invention, and described above, is sufficient protection for cores and molds for many types of castings. However, where extra resistance to heat of the metal is required, the fluid mixture is made to serve as a binder for the finely divided refractory materials commonly used in foundries, such as silica, mica, graphite, zircon, clays, etc., which are mixed into the fluid binder, by simple stirring and the mixture then reduced with water to the required consistency. Such refractory materials are available in a wide variety of types and grades, and when used in admixture with a synthetic resin-oil emulsion combination the latter becomes the vehicle and the binder for the refractory material. These refractory materials are relatively inert chemically and do not destroy the technological properties of the resin dispersion as to collapsibility, penetration, drying and strength described above. Although, drying oils and drying oil alkyd resins have been referred to above as components of the compositions utilized in the present invention, the so called semi-drying oils may be substituted in whole or in part for them; and the expression "drying oil" in the appended

claims is intended to include drying oils, drying oil alkyd resins and semi-drying oils.

For the sake of brevity, the expression "mold surface" in the appended claims is used to designate a part or the parts of a foundry sand mold and the cores inserted therein, if any, with which the molten metal comes in direct contact during the pouring or casting operations; the said expression "mold surface" is therefore used in the appended claims as applying to cores as well as to the sand mold itself.

In our copending case Serial No. 458,034, filed September 11, 1942, we claim a foundry sand mold, a part at least of the surface of which is coated with a coating composition containing an aqueous solution of a condensation product of a phenolic body with formaldehyde.

We claim:

1. A foundry sand mold surface coated with a mixture comprising a water soluble thermosetting synthetic resin condensate and an aqueous emulsion of a drying oil.
2. A foundry sand mold surface coated with a mixture comprising a water-soluble urea-aldehyde condensate and an aqueous emulsion of a drying oil.
3. A foundry sand mold surface coated with a suspension of a refractory material in a liquid vehicle comprising a water soluble thermosetting synthetic resin condensate and a drying oil.
4. In the art of producing castings of metals with sand molds, the process which comprises coating the mold surface of said molds with a mixture comprising a water soluble thermosetting synthetic resin condensate and an aqueous emulsion of a drying oil.
5. In the art of producing castings of metals with sand molds, the process which comprises coating the mold surface of said molds with a mixture comprising a water-soluble urea-aldehyde condensate and an aqueous emulsion of a drying oil.
6. A foundry sand mold surface coated with a mixture comprising a water soluble thermosetting synthetic resin and a drying oil.
7. A foundry sand mold surface coated with a dispersion of a drying oil in an aqueous solution of a water soluble thermosetting synthetic resin.

HAROLD K. SALZBERG.
WALTER B. KINNEY.