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CROSS REFERENCE
EXAMINER

Sept. 10, 1940. A. B. RUDDLE ET AL 2,214,349
COMPOSITION OF MATTER FOR CORES
Filed Feb. 13, 1939 2 Sheets-Sheet 1

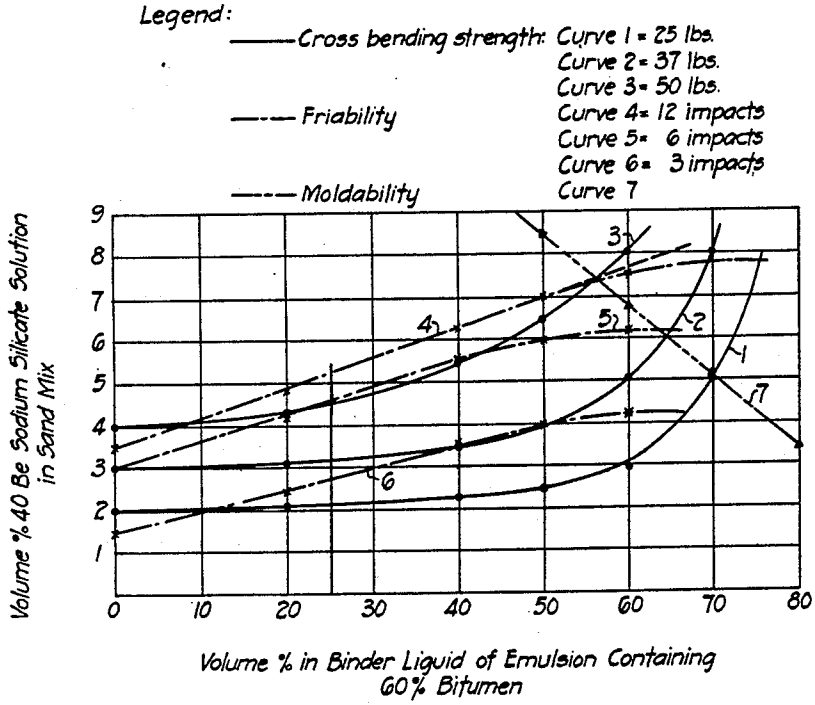


Figure 1

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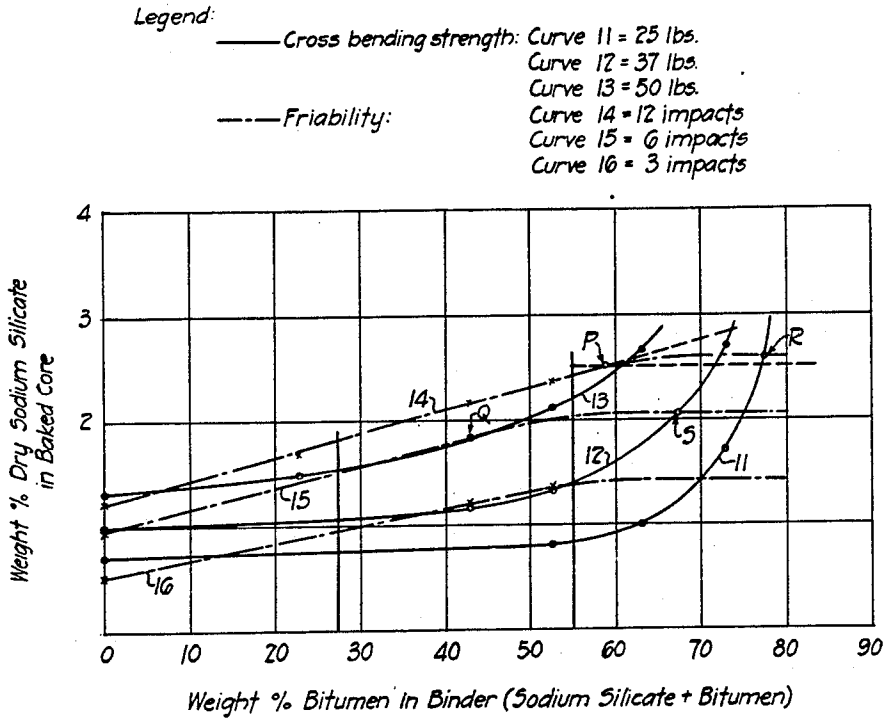


Figure 2

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UNITED STATES PATENT OFFICE

2,214,349

COMPOSITION OF MATTER FOR CORES

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Application February 13, 1939, Serial No. 256,250

3 Claims. (Cl. 22—188)

This invention relates to molded products and a process for making same, which products have as their principal ingredient sand or other similar granular powdery substances capable of withstanding extremely high temperatures without chemical decomposition. More particularly our invention deals with the making of cores used in the casting of molten metals, such as iron, steel, aluminum, etc.

In the art of casting hollow objects, it is customary to prepare a mold which represents a negative of the exact outside contour of the object to be cast. Into this mold there is placed a body called the core, having the inside contour of the object. After properly closing the mold, containing the core, the metal is then poured into the empty space inside the mold through a spout specially provided for the purpose.

Depending upon the size and shape of the object to be cast as well as the metal used, the composition of both the mold and the core is varied widely to meet varying conditions. All molds and cores are prepared from sand or similar high melting chemically inert granular material, which is held together by a suitable binder. To enable shaping of the sand, the binder must be originally liquid, and upon standing and/or heating to moderately elevated temperatures must harden as by evaporation of a solvent for the solid binder, or by polymerization, etc. Later the completed molds and cores, when hardened, must be capable of retaining their shape under the metal-casting conditions for a time at least sufficient, until the metal has cooled to a point of solidification. Upon further cooling, when the solidified hollow object contracts the core must not be so hard to cause the object to crack, but must be sufficiently compressible or friable, to give way to the contracting metal.

There are a variety of other conditions which the mold and/or the core must meet. For example in casting very large objects, such as the block of a marine Diesel engine, or the housing of a hydroelectric turbine, a common difficulty is the washing away or errosion of the mold or the core by the flowing metals in the vicinity of the intake spout. To prevent this, an extremely resistant sand mixture must be used of very high sintering temperature, containing a binder which does not melt, char or otherwise disintegrate under casting conditions. When the object is finally cast and has cooled sufficiently to be taken from the mold, the mold may be broken away by hammering and chiseling. The core, if hard, must likewise be chiseled out, a task which is not difficult when dealing with large objects. However, in small objects, the chiseling out of the core is neither practical nor feasible, and to make the mass production of small objects such as valves, grates, small cylinders ,etc., possible at a reasonable cost, it must be possible to break out the core by merely hammering the object from the outside. In other words the core must be highly friable and shatterable after casting.

Difficulties which cause frequent failures of castings are insufficient porosity of the core and evolution of an excessive amount of gas mostly due to thermal decomposition of the binder. This causes the formation of bubbles in the casting or may prevent the flow of the molten metal through narrow passages in the mold.

From the above it will be observed that no one sand-binder mixture is suitable for all types of castings and the choice of the proper mixture must depend primarily upon the size of the casting and the temperature of the molten metal.

Our invention is primarily concerned with the preparation of relatively small cores, which must possess fair strength after drying or baking at moderately elevated temperatures, so that they can be handled without danger of breaking, in particular if they have long narrow shapes, or carry sharp edges, ridges, and the like which may form an important part in the shape of the casting to be produced. Upon casting these cores should emanate a minimum amount of gas, and their porosity must be sufficient to prevent the building up of substantial gas pressures in the space to be occupied by the metal inside the mold. Later, when the metal has been cast, the core should not at once collapse, but should maintain its shape. But when hammering the cooled casting from the outside, it should fall apart and run out freely.

Innumerable mixtures of sand with different types of binders have been tried, water glass, asphalt, resins, starches, drying fatty oils, lead oxide-glycerine cement, etc., until to-day linseed oil is used almost exclusively for all small cores. The reasons for this development are somewhat difficult to explain, for we have discovered and proven by a large number of experiments that mixtures of water glass and bitumen, if used with certain precautions and within certain limits may provide a binder much superior to linseed oil. We have been able to produce with our mixture, cores which meet all the above requirements and which materially reduce the number of failures, frequently amounting to as much as 15 or 20% of the total number of castings made.

Our preferred core-making composition consists essentially of sand, an aqueous solution of a water soluble alkali metal silicate such as commercial waterglass, and a bituminous material such as asphalt. If the composition is too dry for shaping and molding, an amount of water or other suitable liquid may be added in amounts to give it the desired workability or moldability. While the proper amount of liquid required for good moldability will vary with the porosity and coarseness of the sand, we have found that in general the mixture should contain not more than about 20% and normally less than 17% liquid. The amount of water-soluble silicate added in the form of an aqueous solution, but calculated on a dry basis, may vary between about .7% to 1.2% by weight of the total mixture in the absence of bituminous material and up to about 2.6% in the presence of substantial amounts of bitumen; and the amount of bituminous material may vary from nothing or a mere trace to about 3 times the weight of the added soluble silicate. In order to enable easy distribution of the asphalt throughout the sand mixture, it is preferred to introduce it in the form of an aqueous emulsion.

When the mixture of sand, aqueous silicate solution and asphalt has been shaped to form a core, it is baked in an oven to dry and harden it. Waterglass and similar aqueous silicate solutions form upon drying hard glassy masses and it is obvious that the cores become stronger with increasing content of the soluble silicate. On the other hand, if the silicate content is too high, the cores retain considerable strength after casting of the metal and it may prove difficult, if not almost impossible, to remove them from the finished casting. The addition of bitumen to the core mix has the effect of greatly improving the friability of the core after casting while comparatively little affecting the strength of the core after baking, if used in amounts not greatly exceeding about 2 times the weight of the soluble silicate added. When, however, using quantities of bitumen much in excess of the above amounts, the strength of the baked core begins to diminish materially. On account of this effect of asphalt on the properties of waterglass-bound cores, the maximum permissible amount of the silicate solution in the sand mix increases with increasing asphalt content.

In foundry practice it is usual to evaluate the strength of the cores by a cross bending test, approved by the American Foundry Association, in which the weight is determined that will break a bar shaped of the core mix and baked. The bar, 1" x 1" x 8", is placed on supports 6" apart, and a beam, which is loaded with a shot at the rate of 24 lbs. per minute presses down on the center of the bar between the supports. The weight which breaks the bar is registered. It is generally accepted that for average foundry work a cross bending strength by the above test of 25 lbs. represents the minimum useful limit, although in exceptional cases a somewhat lower strength may be allowable.

We have found that the strength of cores made from sand containing given amounts of an aqueous solution of a soluble silicate as binder, may vary over wide limits depending upon the baking conditions. In particular we have found that CO_2 and other acid gases, such as SO_2, H_2S, etc., have a detrimental influence on the core strength, and that if cores are baked in the presence of CO_2 or other acid gases, the ultimate strength of the core may be but a small fraction of that which would be obtained in the absence of the acid gases under otherwise identical conditions. What apparently happens in the presence of acid gases is a destruction of the soluble silicate, the gaseous acid precipitating free SiO_2, which upon drying forms a powder having no adhesive properties, rather than a glass-like continuous mass. It further appears that the influence of acid gases is more pronounced if the amount of soluble silicate binder is relatively small. It may be that the effect of acid gases is responsible for the fact that soluble silicates, although previously suggested for core making, have never been used on a commercial scale, since normally core baking ovens are fired directly, the flue gases coming in direct contact with the cores. On account of this contact it may have been necessary to use quantities of soluble silicate much in excess of those which will result in good friability, in order to secure sufficient strength of the baked cores, and indeed publications disclosing the use of waterglass for this purpose suggest amounts of the order of 10%. Other factors which affect the strength of the core are temperature and time of baking. Suitable temperatures range from about 250° to 600° F., especially good results being obtainable at about 350–500° F. As to the influence of the time of baking, we have found that a maximum strength is usually reached after a given time which may vary from about 15 minutes to 4 hours, depending upon the size of the core, after which time the strength slowly decreases. Since in practice cores of many different sizes are usually baked in a single oven an average baking time must be used and, consequently small cores may be overbaked and large ones underbaked. Therefore it is desirable to allow a safety factor of about 50% above the minimum approved strength of 25 lbs., and work on the premise that sand mixtures should be used only, capable of yielding cores having cross bending strengths of not less than 37 lbs. by the American Foundry Association test.

In order to determine the friability or shatterability of the core after casting, we have evolved a test comprising heating a 1" cube of the core to be tested in a substantially closed container in a muffle oven to 1750° F. for 30 minutes. Temperature measurements in cores used in actual casting of iron and steel indicated that this is fairly representative of the heating to which cores are usually exposed during casting. The heated cube is allowed to cool and is then placed on a steel plate. A flat cover of steel,

$$1'' \times 1'' \times \tfrac{5}{16}''$$

(weight 54 grams), is placed on the test piece and a plunger of 100 gr. weight is allowed to drop onto the cover from a height of exactly 4 cm. The number of impacts required to shatter the test piece is an indication of its friability. Comparison with foundry tests have proven that a friability of 12 impacts represents the upper practical limit, and that for satisfactory friability the number of impacts causing shattering should be 6 or less by the above shatter test.

Cores made of sand, silicate solution and asphalt, in order to meet the above requirements of cross bending strength and shatterability must have compositions within very narrow limits. These limits are shown in the attached drawings, which represent composition of graphs, Figure 1 showing the composition of the sand mix used for molding the cores, in terms of volume per cent

of sodium silicate solution in the sand mix, and volume per cent asphalt emulsion in the binder. Figure 2 shows the compositions of Figure 1 after baking, i. e. after elimination of the water of solution and emulsion, all percentages now being expressed in weight percent. It will be seen, the figures contain several families of curves. One family of curves (1—3 and 11—13 in Figures 1 and 2 respectively) connects points of equal cross bending strengths of the baked cores; another family (4—6 and 14—15 respectively) connects points of equal shatterability or friability of the cores after casting of the metal.

Referring to Figure 1, on the ordinate of the graph is plotted the content of silicate solution in the sand mix, the content being expressed for convenience in volume per cent of a 40° Bé. sodium silicate solution contained in the total sand mixture, the average sand used in core making having an apparent density of 1.55. On the abscissa is indicated the volume per cent of asphalt emulsion in the binder which consists of 40° Bé. sodium silicate solution and asphalt emulsion, added to the dry sand, the emulsion containing 60% bitumen. Curves 1—3 bending upward indicate the cross-bending strength by the American Foundry Association test hereinbefore described, of cores baked under optimum conditions and in the absence of acidic gases. Curves marked 4—6 respectively stand for the shatterability of the cores after casting, in terms of the described shatter test. Curve 7 connotes the moldability limit of the sand mix imposed by the maximum permissible content of liquid, normally equal to 17% by volume as stated earlier. It will be observed that the composition of sand mixes which are suitable for core making fall within an area on the plot enclosed between the ordinate and the curves 1, 7 and 4. If any one of the limitations, for which these curves stand, are transgressed, the resulting core will be unsatisfactory. A preferred area is enclosed by curves 2 and 5, compositions represented by this area giving cores having a fair margin of safety in the cross bending strength, should baking conditions be other than optimum as is the rule in foundry practice, and also having a shatterability which insures easy removal of the core from the casting.

The several curves which represent the limits of usefulness and preferred range respectively, in the composition of the sand mixes can be expressed in terms of algebraic equations, X being the abscissa and Y the ordinate, both in the scales hereinbefore indicated. Curve 4, is substantially a straight line between the ordinate and the point of intersection with curve 7. Above this point it flattens out to reach a ceiling of $y=7.7$. Below this point it has the equation:

$$7x-100y+350=0$$

Curve 5, although slightly curved in the upper part reaching a ceiling of 6.1, approximates a straight line:

$$x-16y+48=0$$

Curve 1 is represented by:

$$11xy-19x-840y+1680=0$$

Curve 2 is:

$$2xy-5x-150y+450=0$$

and curve 7 equals:

$$7x+40y-690=0$$

While in preparing the sand mix it is not necessary to use 40° Bé. alkali metal silicate solution, nor a 60% asphalt emulsion, it is convenient to use the soluble silicate and asphalt in the form of aqueous solutions and emulsions, respectively, having these approximate concentrations, since they are commercially available. It being known that 40° Bé. sodium silicate solution contains about 38% dry sodium silicate, solutions of different concentrations to give the same results may readily be substituted to meet the limitations indicated by the equations. Moreover the asphalt need not be used as an emulsion but may be mixed with the sand in any convenient manner which produces fine distribution of the asphalt throughout the sand mix. Manifestly, however, by employing emulsions this result can most easily be achieved. On the other hand when using pulverized asphalt there is less likelihood of using too large an amount of liquid which would make the sand mix too wet for good moldability.

In the course of the baking process, the core is more or less thoroughly dried so that it is composed essentially of sand, glassy water soluble silicate and asphalt. The limits within which the proportions of these three components must fall to insure sufficient cross-bending strength and shatterability after casting, are shown in Figure 2, which is essentially Figure 1 reduced to the anhydrous state and changed to a weight per cent scale. The several curves which limit the useful and preferred ranges of compositions of the cores may now be expressed by the following equations; x being the weight percent of bitumen of the binder consisting essentially of dry sodium silicate and bitumen, and y being the weight percent of the dry sodium silicate in the mixture of sand, sodium silicate and asphalt.

Curve 14 (corresponding to curve 4 in Figure 1) is substantially a straight line up to point P ($x=59$) and then flattens out to reach a ceiling of $y=2.6$. Below P, it follows the equation:

$$11x-450y+495=0$$

Curve 15 (corresponding to curve 5 in Figure 1) is a straight line below point Q ($x=45$) and then flattens out to reach a ceiling of $y=2.05$. Below Q, it has the equation:

$$9x-400y+400=0$$

Curve 11 (corresponding to curve 1 in Figure 1) is

$$5xy-3x-420y+294=0$$

and curve 12 (corresponding to curve 2 in Figure 1)

$$11xy-9x-875y+875=0$$

Cores having compositions represented by the area bounded by curves 11 and 14 as expressed in the above equations and having a water soluble silicate content not above 2.5% by weight are within the operative range. For reasons explained before, however, it is preferred that the composition fall within an area limited by curves 12 and 15 and have a content of water soluble silicate not over 2.05%. It may further be noted that the content of bitumen in the binder should never exceed 77% by weight on a dry basis, and preferably should be below 67% as indicated by points R and S, respectively.

Inasmuch as it is desirable to obtain baked cores having a maximum strength for a minimum number of impacts required to shatter the core after casting, it appears that a portion of

the useful area in the graphs in which the shatterability curves rise highest over the strength curves indicates an optimum range. As will be seen in Figure 1 such a range exists over the area in which the volume percent of asphalt emulsion in the binder solution ranges from about 25 to 50%. The corresponding range in Figure 2 extends approximately from 30 to 60% by weight of asphalt in the dry binder. To take advantage of this optimum relation between cross-bending strength and shatterability, we prefer to limit our composition to the optimum ratio of asphalt to binder indicated above.

The preparation of the sand mix for making the core is exceedingly simple. The liquids are simply mixed with the sand in the desired proportions either by hand or mechanically, and if the mix appears too dry for molding, water may be added to suit convenience. The order of adding the alkali metal silicate solution and asphalt to the sand is relatively unimportant. Either component may be added first, or both may be added simultaneously, if desired in the form of a prepared emulsion containing the alkali metal silicate and bitumen in the preferred proportion.

In the foregoing disclosure we have repeatedly used the term soluble alkali metal silicate. By this term we mean a water soluble alkali metal silicate, such as waterglass which may contain varying amounts of free alkali metal hydroxide. As is known, commercial waterglass which is essentially an aqueous solution of sodium silicate, comes in various grades of varying ratios of $Na_2O:SiO_2$. While any of the several commercial grades may be used, we prefer to employ those having relatively high SiO_2 contents, i. e., relatively low free alkalinity, because high alkalinity has an irritating effect on the skin of the workers who shape the cores and necessarily come in direct contact with sand mix. By selecting a waterglass solution containing SiO_2 and Na_2O in ratios above about 3.0, we have been able to handle our mix over extended periods of time with no apparent ill effect.

Furthermore the aqueous alkali metal silicate solution may contain small quantities of other salts, in particular salts which slowly tend to absorb a portion of the free alkali. Salts having this property are for example the fluosilicates, which are decomposed by free alkali, thereby liberating alkali fluorides and precipitating a silicate of low alkali content which is substantially insoluble in water. This absorption of free alkali has a tendency to cause the sand mix to set and to make it less hygroscopic after baking, a property which may be of considerable importance in moist climates. For example the addition ½ to 5% sodium fluosilicate to a 40° Bé. waterglass solution used in preparing the mix, may have this effect. If desired small amounts of salts of weak bases and strong acids may be added, such as aluminum sulfate, ammonium chloride, magnesium chloride, etc., which also absorb free alkali and simultaneously may precipitate small amounts of water insoluble hydrated silicates, which upon baking seem to make the core even more resistant against attack by moisture. It stands to reason however that the amounts of the addition salts should be so proportioned, that only a portion of the alkali of the soluble silicate is removed. Otherwise free SiO_2 is liberated which, as previously pointed out, has little or no binding power. For example, we may prepare a soluble silicate solution as follows:

Water	gallons	2
Aluminum sulfate	ounces	1–10
Alkali fluosilicate	do	1–10
Waterglass 40° Bé. ($Na_2O+3.3SiO_2$)	gals.	1–10

The above solution may be mixed with sand and asphalt emulsion as follows:

	Volume per cent
Sand (dry)	91.4
Solution	6.5
Emulsion (containing 60% asphalt)	2.1
Water to suit moldability of mix.	

The bitumen which we employ may be a straight run or cracked petroleum residue, or a coal tar product. It may contain suspended carbon or other impurities. A portion or all of the bitumen may be substituted by other high boiling organic substances which are chemically substantially inert to water soluble silicates at normal room temperatures and under the conditions of baking such as various types of resins, particularly petroleum resins or plastics, lubricating oils, poly alcohols e. g. glycerine, sugars, dextrins, starches, etc., which do not substantially evaporate or decompose under the conditions of baking, but carbonize at the temperature of casting. However, bituminous materials are preferred because they evolve the least amount of gas during casting since they contain an extremely high ratio of carbon to hydrogen or other elements potentially forming gaseous compounds upon heating.

We claim as our invention:

1. The process of making cores with adequate strength and sufficient friability for foundry practice, which comprises preparing a mixture of sand, an aqueous solution of a water soluble silicate, and a bitumen, said mixture containing sufficient normally liquid components to make it moldable, the amount of the silicate being from 1.2% to 2.6% dry basis, and the amount of the bitumen being not more than three times the weight of the silicate, and baking said mixture to substantial dryness in an atmosphere substantially free from acidic gases at a temperature below 600° F.

2. The process of making cores with adequate strength and sufficient friability for foundry practice, which comprises preparing a mixture of sand, an aqueous solution of sodium silicate, and a bitumen, the amount of said silicate being from 1.2% to 2.6% dry basis, and the amount of said bitumen being not more than three times the weight of the silicate, and baking said mixture in an atmosphere substantially free from acidic gases.

3. The process of making cores with adequate strength and sufficient friability for foundry practice, which comprises preparing a mixture of sand, an aqueous solution of a water soluble silicate including a small quantity of fluosilicate, and a bitumen, said mixture containing sufficient normally liquid components to make it moldable, but not more than 17% thereof, and baking said mixture in an atmosphere substantially free from acidic gases at a temperature below 600° F.

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