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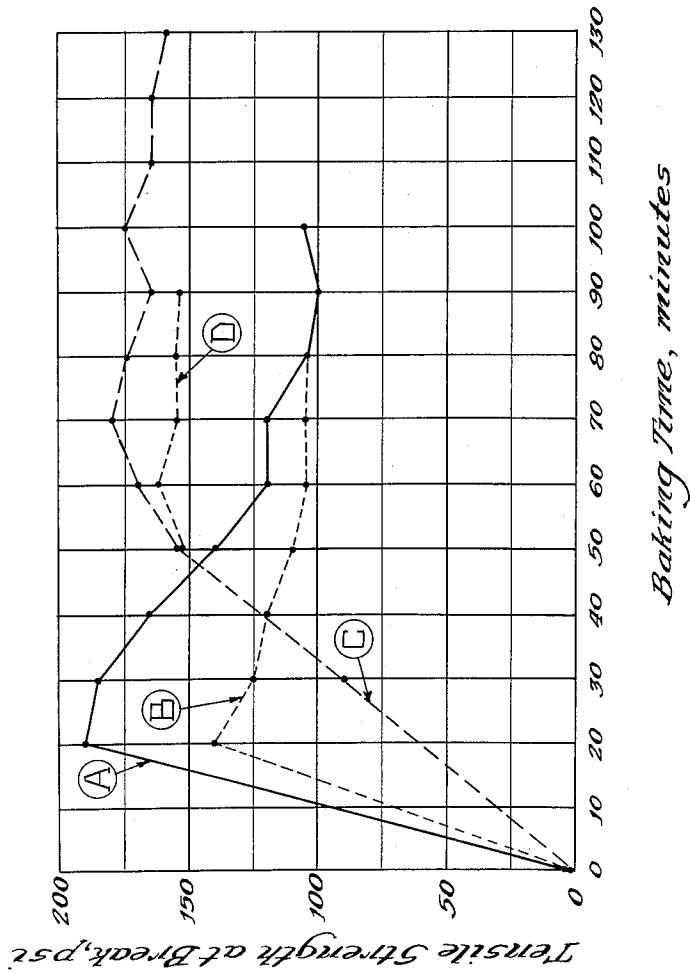
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2,977,236

CORE BINDER

Filed Dec. 30, 1957

Phosphate-modified starch
A. *(A)+ cereal*
B. *(A)+ core oil*
C. *Standard cereal-oil binder*
D.



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2,977,236

CORE BINDER

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4 Claims. (Cl. 106—38.5)

The present invention relates to foundry cores. More particularly, it relates to an improved foundry core containing a binder having superior properties.

A foundry core has been defined as an aggregate of inert matter such as sand, having a degree of porosity and a controlled mechanical strength sufficient to allow the core to be assembled without breakage as a part of a mold and to form molten metal into a desired shape. For this purpose, it is necessary to incorporate in the sand a material or materials to bind the sand together and to give it the desired mechanical strength. Numerous materials have been used for this purpose in the past, including cereal products, water glass, drying oils, resins, sulfite liquor, proteinaceous materials, molasses, clays, wood flour, gelatinized starches, dextrinized starches, and many other substances and combinations thereof. All of these materials have their points of superiority and inferiority, depending upon the particular type of sand employed, the type of metal to be cast, the size of the casting, the precision required, and other factors disclosed in the art. The present invention involves the use of a novel type of core binder, either alone or in combination with other binding materials, whereby cores of superior properties are obtained.

One object of the present invention is to prepare a foundry core having improved properties.

Another object is to provide an improved binding material for foundry cores.

Another object is to provide a core binding material of versatile properties, adaptable to use in the preparation of cores having special characteristics.

Other objects of the invention will be apparent from the present description and claims.

In accordance with the present invention, I employ as a foundry core binder an alkali-metal phosphate-modified starch, prepared as described hereinafter. The phosphate-modified starch is preferably employed in the form of a dry powder, which is suitably mullied or otherwise blended into a core sand in a proportion between about 0.1 and about 3% by weight, optimally around 0.5 to 1.5% based on the dry mixture. Water is also added to the sand and blended therein, preferably before addition of the phosphate-modified starch, the final proportion of water being suitably between about 2 and about 6% by weight, preferably between about 3 and about 5%. Alternatively, the phosphate-modified starch can be added to sand, if desired, in the form of an aqueous dispersion or paste. Other materials of the types commonly employed as core binders may also be incorporated in the core mixture as desired. Thereafter, the mixture is formed into cores in the conventional manner, after which the core is baked or cured under conventional conditions prior to use.

In baking cores, the temperature and time required vary widely according to the size of the core, the surface-to-volume ratio, the water content, the type of sand, and the nature of the core binder. Laboratory cores are baked at temperatures between about 300 and about 600° F., and baking times of about 10 to about 100 minutes are required to reach maximum tensile strength. The baking temperature is preferably between about 350 and about 450° F., and for small cores containing my improved binder, a baking time of around 10 to 30 minutes is ordinarily sufficient. For commercial cores, the bak-

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ing time may range up to 24 hours, and temperatures up to 600° F. are sometimes used to speed up to process.

The preparation of alkali-metal phosphate-modified starches suitable for use in my invention is described in my U.S. Patents 2,884,412 (April 28, 1959) and 2,865,762 (December 23, 1958). In the described method, starch is impregnated with a solution of an alkali-metal phosphate salt, then dried and heated at a temperature between about 120 and about 175° C., whereby desirable changes are produced in the properties of the starch. In one representative example, dried, ungelatinized starch is immersed in an aqueous solution of an alkali-metal orthophosphate, the liquid phase is removed, the impregnated starch is dried to less than about 15% moisture at a temperature below its gelatinization point, and the dried starch-phosphate mixture is heated for around 1 to 15 hours at about 130 to about 170° C., preferably about 5 hours at about 160° C., the length of the heating period varying inversely with the temperature. A modified starch is obtained thereby having the property of dispersing rapidly in cold water to produce dispersions having a viscosity between about 1,000 and about 5,000 cp., measured in 5% aqueous solution at room temperature.

As defined in my U.S. Patent 2,884,412, the starch phosphates employed in my invention are substances prepared by impregnating an ungelatinized starch with at least about 1.0% by weight, calculated as phosphorus, of at least one phosphate salt of an alkali-metal in an aqueous solution of said salt having a pH between 3.0 and about 7.5, and heating the impregnated starch in the substantial absence of unabsorbed water at a temperature between about 120 and about 175° C. for a period of about 1 to about 15 hours.

Preferred phosphate salts are sodium, potassium, and lithium orthophosphates, alone or in suitable combinations to yield a pH in aqueous solution between about 4 and about 7, preferably around 6, measured at 25° C. at the concentration employed. For example, monosodium orthophosphate and disodium orthophosphate are combined in aqueous solution in such proportions as to produce a pH between about 6 and about 7. Or the desired salts may be formed in situ, for example, by dissolving trisodium orthophosphate or other basic phosphate salt in water and adjusting the pH of the solution to the desired level by adding orthophosphoric acid or an acidic orthophosphate salt. Alternatively, orthophosphoric acid or an acidic phosphate in aqueous solution may be adjusted upward to the desired pH by adding an alkali-metal hydroxide or a basic alkali-metal orthophosphate salt.

The phosphate solution may suitably be between about 1 and about 3 molar in phosphate and should be used in a quantity equivalent to at least about 1% by weight of phosphorus, preferably between about 3 and about 5%, based on the quantity of starch to be treated. The quantity and concentration of solution should be chosen so that the starch will form a slurry when commingled therewith. The quantity of starch will generally be less than 1.5 times the weight of the water contained in the solution, and will preferably be less than the weight of water. The slurry should be agitated or stirred for 5 to 10 minutes or more to permit the starch granules to become soaked with the solution.

The soaked starch granules are separated from the solution by filtration, centrifugation, or the like, and the liquid phase is largely removed, suitably by air drying at a temperature below the point at which starch gelatinizes, e.g., below about 60 to 80° C., depending upon the particular starch. The resulting granules, which generally contain between about 8 and about 15% of water, are subjected to a heat treatment as set forth hereinabove. The heat-

treated material is a phosphate-modified starch suitable for use as a core binder or a core-binder component in accordance with my invention.

The phosphate-modified starches prepared as described above can be fractionated if desired to separate a material yielding dispersions of higher viscosity according to a technique described by Jacob W. Sietsema and William C. Trotter in copending application Serial No. 637,351, filed January 31, 1957. In accordance with the Sietsema-Trotter technique, a phosphate-modified starch is dispersed in water in a proportion between about 1 and about 15% by weight or higher up to the saturation level, based upon the quantity of water employed, and a fraction thereof is precipitated by adding an oxygen-containing water-miscible organic liquid, such as methanol, acetone, or the like, in a proportion sufficient to produce a mixed solvent containing between about 35 and about 65% by volume of the added organic liquid. The precipitate is separated from the liquid phase, and preferably dried. This material contains a decreased proportion of inorganic phosphates, color bodies, and other impurities, and aqueous dispersions thereof are substantially higher in viscosity than comparable dispersions of the starting material.

Cores prepared according to my invention have normal green strength, breaking at a tensile strength around 1 p.s.i. Surprisingly, I have found that the green strength can be markedly improved, if desired, by addition of certain inert fines, such as fine sand, silica flour, olivine flour, iron-oxide fines, and the like. Such mixtures also exhibit the unusual property of increased baked strength. Moreover, I have further found that my new cores can be improved in both green strength and hot strength by adding certain carbonaceous materials, such as pitch and sea coal. All of these additives, it should be noted, are highly detrimental when used with conventional core binders.

My new type of core exhibits the remarkable property of baking equally fast with either high or low proportions of binder. Thus, overbaking may occur when the cores are made with open sands, which themselves tend to bake faster and to require less moisture. With such sands, it is desirable to reduce the baking time, to increase the moisture content, or to add a humectant such as glycerin or sorbitol; the simplest expedient, however, is to introduce a quantity of fine sand or flour. Angular sands bake even more rapidly, and require the closest control. With all open or angular sands, an increased proportion of cereal is desirable, together with a smaller proportion of phosphate-modified starch.

I have observed that cores containing my new binder are more resistant to humid atmospheres than cores made with oil binders. Nevertheless, the bond produced by my binder is water-soluble; and when a core made therewith is immersed in water, it disintegrates. This is seldom a problem in commercial operations; but where it is, the problem can be avoided in a simple manner by incorporating a water-repellent material such as a silicone or other material known to the art.

The following specific examples will more clearly illustrate my invention. All of the tests described therein were carried out according to standard methods defined in the "Foundry Sand Handbook," sixth edition (1952), published by the American Foundrymen's Society, Chicago. All measurements are on dry basis. In each case, the cores were prepared and tested in triplicate, and the reported results are the average of the three tests.

Example 1

A series of tests were carried out to compare cores containing phosphate-modified corn starch alone, phosphate-modified corn starch in combination with cereal and with a core oil, and a conventional binder comprising cereal, oil, and clay. The phosphate-modified starch was a high-viscosity material having a viscosity above 100,000 cps. at 25° C., measured in 5% aqueous dispersion, and was obtained by methanol precipitation from an aqueous

dispersion of phosphate-modified starch according to the technique described above. The sand employed was No. 1 steel sand having an AFS grain fineness of 65 ("AGF 65"). The core mixtures were prepared as follows:

A. Phosphate-modified starch alone:

1% phosphate-modified starch
5.5% water

Remainder sand

The dry ingredients were milled 1 minute in a laboratory-size Simpson muller, the water was added, mulling was continued for 6 minutes, and the mixture was discharged and stored in a sealed can until used to make cores. The retained water content was 5.1%.

B. Cereal added:

1% phosphate-modified starch
1% corn cereal ("Truscor")
0.3% southern bentonite
5.5% water

Remainder sand

The mixture was milled as before. The retained water content was 5.5%.

C. Core oil added:

1% phosphate-modified starch
0.25% core oil
0.125% kerosene
0.3% southern bentonite
6% water

Remainder sand

The dry ingredients were milled 1 minute. The water was added and milled 1 minute. The core oil was added and milled 5.5 minutes. The kerosene was added and milled 0.5 minute. The completed mixture was discharged and stored. It retained 5.6% water.

D. Standard cereal-oil binder:

1% corn cereal ("Truscor")
1.25% core oil
0.125% kerosene
0.3% southern bentonite
3% water

Remainder sand

The dry ingredients were milled 1 minute. The water was added and milled 3 minutes. The core oil and the kerosene were added together and milled 3 minutes. The completed mixture was discharged and stored. It retained 3% water.

The various mixtures were formed into standard test cores and found to have green strengths (tensile strength at break, before baking) as follows:

	P.s.i.
A	1.2
B	4.2
C	1.1
D	0.76

Test cores were then baked at 425° F. over a series of baking periods, and were found to have baked strengths as follows:

Baking Time, min.	Tensile Strength at Break			
	A	B	C	D
65				
20	190	140		
30	185	125	90	
40	165	120		
50	140	110	155	153
60	120	105	170	162
70	120	105	180	155
80	105	105	175	156
90	100	100	165	154
100	105		175	
110			165	
120			165	
130			160	

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The foregoing data are plotted in the attached drawing. From the curves contained therein, it will be observed that phosphate-modified starch, when used alone as a binder (curve A), produced a core which was stronger than the typical prior-art cereal-oil-clay combination (curve D), and reached maximum strength in only 20 minutes, compared with 50 minutes for a similar core containing oil. The phosphate-modified starch was compatible with core oil and with cereal, and could be used to improve one or more of the properties thereof. The inclusion of clay in cores containing phosphate-modified starch appears to be contra-indicated.

The core mixtures were then tested for "hot strength," measured in terms of the time required by a $\frac{1}{8}$ " dia. x 2" cylindrical test core to collapse under a 100 lb. load at a given oven temperature. In each case the test cores were baked for a time known to give approximately the maximum hot strength. For this purpose, the specimens containing core oil required 70 minutes at 425° F., while the other specimens required only 20 minutes. The test results were as follows:

Oven Temperature, ° F.	Time for Collapse at 100 lb. Load, min.			
	A	B	C	D
800.....	2.59	3.20	3.20	
1,000.....	1.75	1.60	2.72	1.37
1,500.....	0.60	0.67	0.93	0.82
2,000.....	0.58	0.47	0.52	0.49

These data demonstrate that my new binder imparts satisfactory hot strength to cores.

Example 2

The following test illustrates the use of a technical-grade phosphate-modified starch, prepared as described above, containing about 4.04% phosphorus and having a viscosity of 6310 cp. at 25° C. in 5% aqueous dispersion.

No. 1 steel sand, AGF 65, was milled with 5% water for 1 minute; then 1.25% of the phosphate-modified starch was added, and mulling was continued for 6 minutes. Standard test cores prepared therefrom had a green strength of 1.15 p.s.i. When baked at 425° F. their strength was as follows:

Baking time, min.:	Baked strength, p.s.i.
15	235
20	230
25	210

Hot-strength test cores, baked 20 min. at 425° F., had the following properties:

Oven temp.:	Time for collapse, min.
800° F.	9.14
1000° F.	5.92
1500° F.	1.31

Example 3

The following test illustrates the combination of cereal with my new core binder material. The mixed core binder comprised corn flour and the technical-grade phosphate-modified starch employed in Example 2.

No. 1 steel sand, AGF 65, was milled with 5% water for 1 minute; then 1% of corn flour and 0.25% of the phosphate-modified starch were added, and the mulling was continued for 6 minutes. The completed mixture contained 5.1% of water. Standard test cores prepared therefrom had a green strength of 1.05 p.s.i. When baked 20 minutes at 425° F., their tensile strength at break was 230 p.s.i.

Hot-strength test cores, baked 20 min. at 425° F., collapsed at the end of 2.79 minutes at an oven temperature of 800° F.

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Example 4

A comparative test showed that a conventional oil-cereal core lost 23% of its baked strength when stored at 100° F. for 16 hours at 100% humidity. A comparable phosphate-modified starch core lost only 8%.

My invention can suitably employ alkali-metal phosphate-modified starches of a wide variety, including those prepared from potato starch, corn starch, wheat starch, cassava starch, arrowroot starch, and the like. The starches should not be subjected to gelatinization, dextrinizing, or other treatment prior to phosphate modification which would materially alter or destroy the essential characteristics of the starch molecule. For this reason, after the starch has been soaked in phosphate solution, it should be dried to less than 15% moisture content before being heated to a temperature above the gelatinization point. If this is not done, the starch undergoes gelatinization and perhaps other forms of degradation during the heat treatment, and a modified starch of inferior properties is obtained.

My cores can be prepared from fine sand with no loss in strength. They bake satisfactorily over a wider range of temperatures than cores containing oil as a binder. They bake in one-half to two-thirds the time of the fastest oil or resin core, or one-third to one-fourth the time of an ordinary oil core. They have high baked strength, in the range of around 175 to 200 p.s.i. or higher at the 1% level, equivalent to 1.25% linseed oil plus 1% of cereal. They have excellent retention of strength when stored in humid atmospheres. Finally, they exhibit low gas evolution, only about one-third as much as a conventional oil-cereal mixture of equal strength.

It is to be understood that the various starting materials, manipulative techniques, process conditions, and other exemplary matter disclosed hereinabove are intended to be illustrative only and not as a limitation upon the scope of the invention. Numerous modifications and equivalents of the invention will be apparent from the foregoing description to those skilled in the art.

This application is a continuation-in-part of my application Serial No. 378,666, filed September 4, 1953, which issued as U.S. Pat. 2,884,412 on April 28, 1959.

In accordance with the foregoing description, I claim as my invention:

1. In the preparation of a foundry core, the improvement which comprises commingling sand with water in a proportion affording a water content between about 2 and about 6% by weight and between about 0.1 and about 3% by weight of an alkali-metal phosphate-modified starch, prepared by soaking dry, ungelatinized starch in an aqueous alkali-metal orthophosphate solution having a pH between about 4 and about 7 to incorporate said alkali-metal orthophosphate therein in a proportion equivalent to at least about 1% by weight of phosphorus, dry basis, removing surface moisture from the starch, drying the starch to a moisture content less than about 15% by weight at a temperature below the gelatinization point thereof, baking the dried starch at a temperature between about 120 and about 175° C. for a period of about 1 to about 15 hours, the length of the baking period varying inversely with the temperature, forming the resulting mixture into the desired shape, and baking the shaped mixture at a temperature between about 300 and about 600° F.

2. In the preparation of a foundry core, the improvement which comprises mulling sand with water in a proportion affording a water content between about 2 and about 6% by weight, adding thereto and mulling therewith between about 0.5 and about 1.5% by weight of a sodium phosphate-modified starch prepared by immersing a dry, ungelatinized starch in an aqueous solution of a sodium orthophosphate having a concentration between about 1 and about 3 molar in phosphate and having a pH between about 4 and about 7 to incorporate

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said sodium orthophosphate therein in a proportion equivalent to at least about 1% by weight of phosphorus, dry basis, removing the liquid phase from the starch, drying the starch to a moisture content less than about 15% by weight at a temperature below the gelatinization point thereof, baking the dried starch at a temperature between about 130 and about 170° C. for a period of about 1 to about 15 hours, the length of the baking period varying inversely with the temperature, forming the resulting mixture into the desired shape, and baking the shaped mixture at a temperature between about 300 and about 600° F.

3. In the preparation of a foundry core, the improvement which comprises mulling sand with water in a proportion affording a water content between about 2 and about 6% by weight, adding thereto and mulling therewith between about 0.5 and about 1.5% by weight of a sodium phosphate-modified starch prepared by immersing a dry, ungelatinized starch in an aqueous solution of a sodium orthophosphate having a concentration between about 1 and about 3 molar in phosphate and having a pH around 6 to incorporate said sodium orthophosphate therein in a proportion equivalent to between about 3 and about 5% by weight of phosphorus, dry basis, removing surface moisture from the starch, drying the starch to a moisture content less than about 15% by weight at a temperature below the gelatinization point thereof, and baking the dried starch for a period of around 5 hours at a temperature around 160° C., forming the resulting mixture into the desired shape, and baking the shaped mixture at a temperature between about 300 and about 600° F.

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4. In the preparation of a foundry core, the improvement which comprises commingling sand with water in a proportion affording a water content between about 2 and about 6% by weight and with between about 0.1 and about 3% by weight of an alkali-metal phosphate-modified starch, prepared by impregnating an ungelatinized starch with at least about 1.0% by weight, calculated as phosphorus, of at least one phosphate salt of an alkali metal in an aqueous solution of said salt having a pH between 3.0 and about 7.5, and heating the impregnated starch in the substantial absence of unabsorbed water at a temperature between about 120 and about 175° C. for a period of about 1 to about 15 hours, the length of the heating period varying inversely with the temperature, forming the resulting mixture into the desired shape, and baking the shaped mixture at a temperature between about 300 and about 600° F.

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UNITED STATES PATENT OFFICE
CERTIFICATION OF CORRECTION

Patent No. 2,977,236

March 28, 1961

Hans Neukom

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 2, line 2, for "up to process" read -- up the process --; column 5, line 14, for "1/8" read -- 1 1/8 --.

Signed and sealed this 29th day of August 1961.

(SEAL)

Attest:

ERNEST W. SWIDER

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Commissioner of Patents