

- [54] **HYDRAULIC CEMENT AND METHOD OF PRODUCING SAME**
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Related U.S. Patent Documents

Reissue of:

- [64] Patent No.: **3,861,928**
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U.S. Applications:

- [63] Continuation-in-part of Ser. No. 85,776, Oct. 30, 1970, Pat. No. 3,682,669, which is a continuation-in-part of Ser. No. 70,596, Sep. 8, 1970, abandoned, which is a continuation of Ser. No. 652,275, Jul. 10, 1967, abandoned.

- [51] Int. Cl.³ **C04B 7/02**
- [52] U.S. Cl. **106/89; 106/100**
- [58] Field of Search **106/89, 100**

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[57] **ABSTRACT**

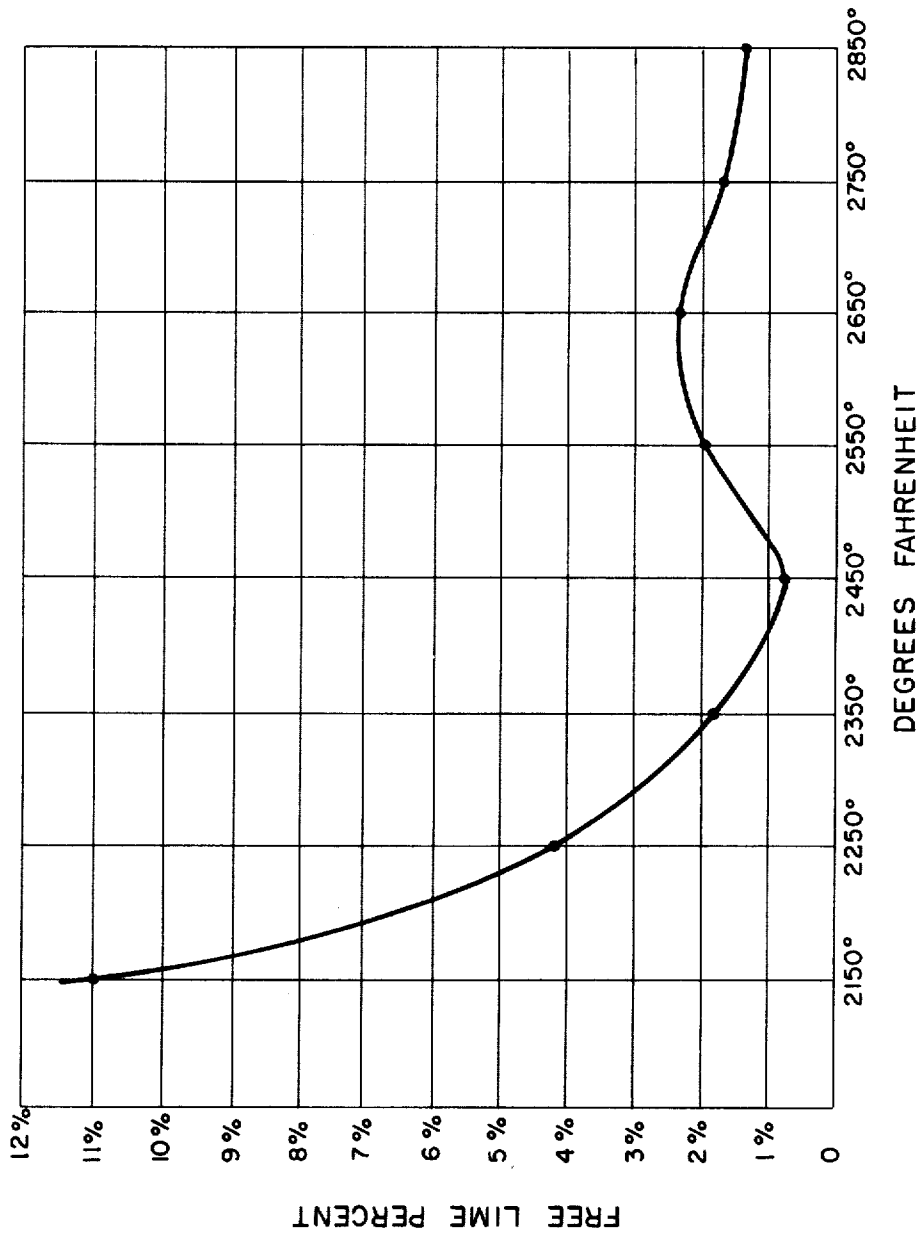
Ground mixtures of conventional Portland cementmak-

ing components are mixed with relatively small amounts of boron-containing components, and the mixtures are burned at kiln temperatures substantially below those normally utilized to form clinker. The [resultant clinker is more easily grindable than that produced in conventional processes of Portland cement production, and the] cement resulting from the grinding of the clinker yields cementitious products possess-

ing substantially higher compressive strength than is exhibited by Portland cement made from the same components in the absence of the boron-containing component.

33 Claims, 6 Drawing Figures

FIG. 1



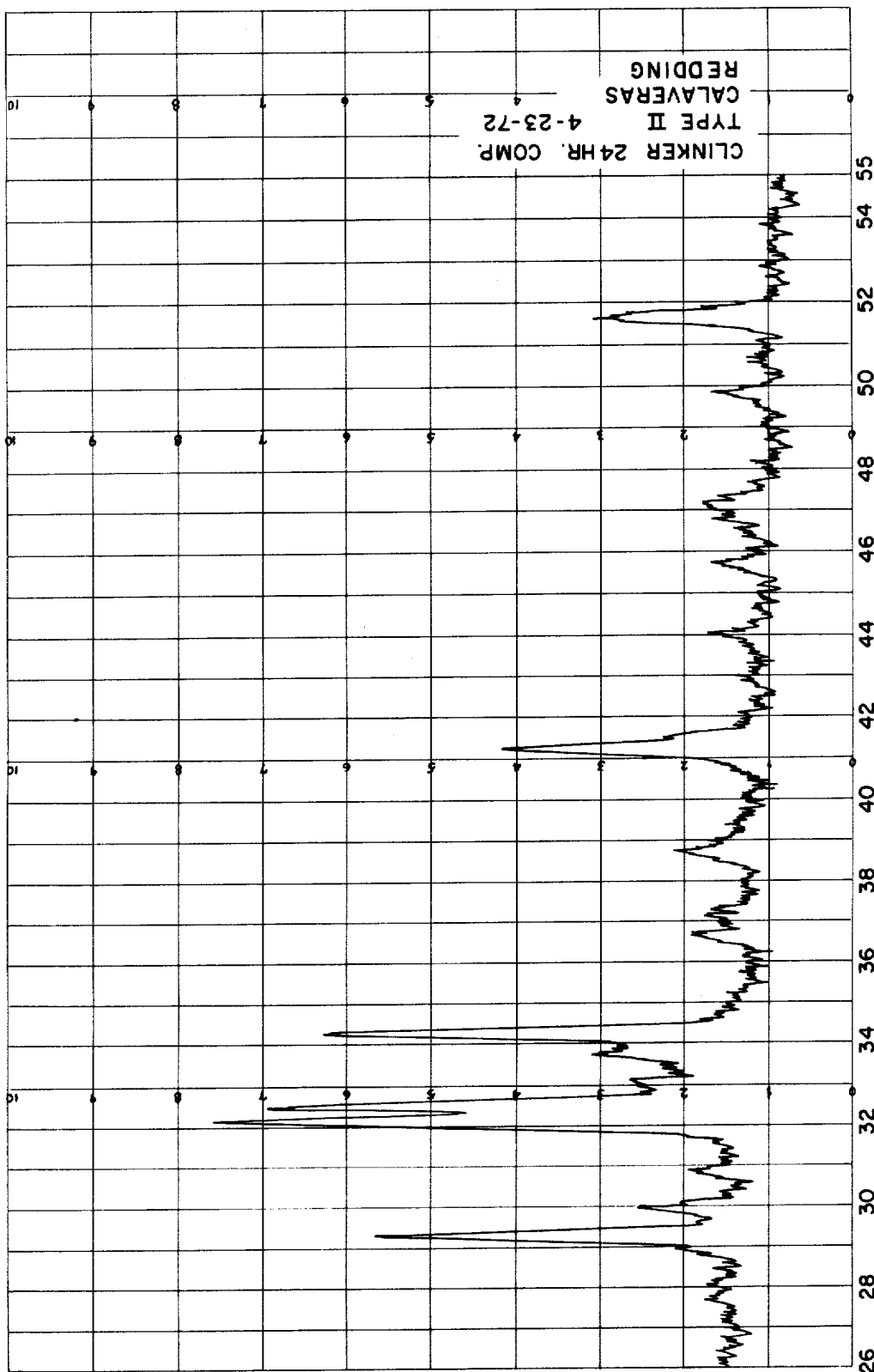


FIG. 2

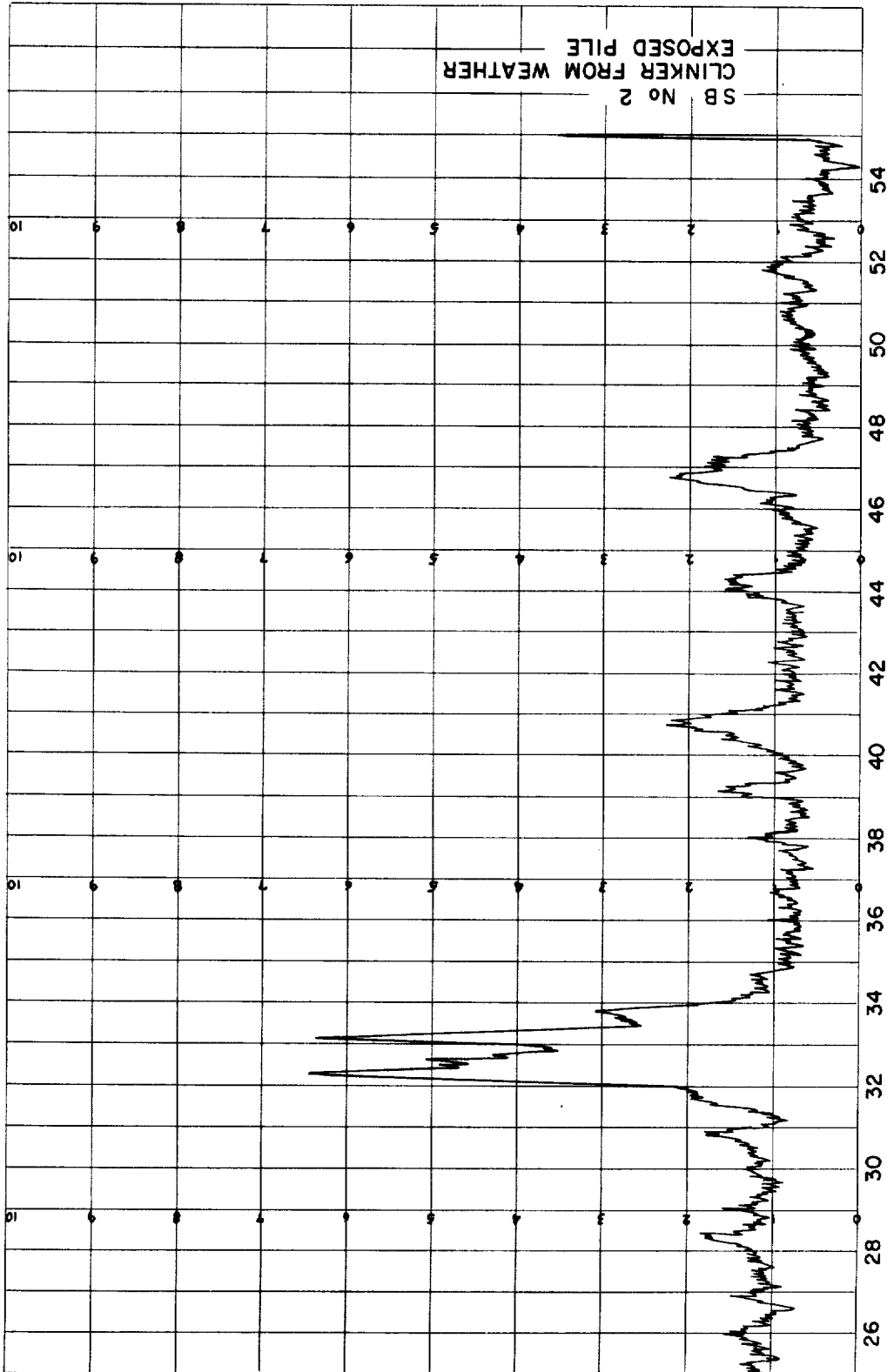


FIG. 3

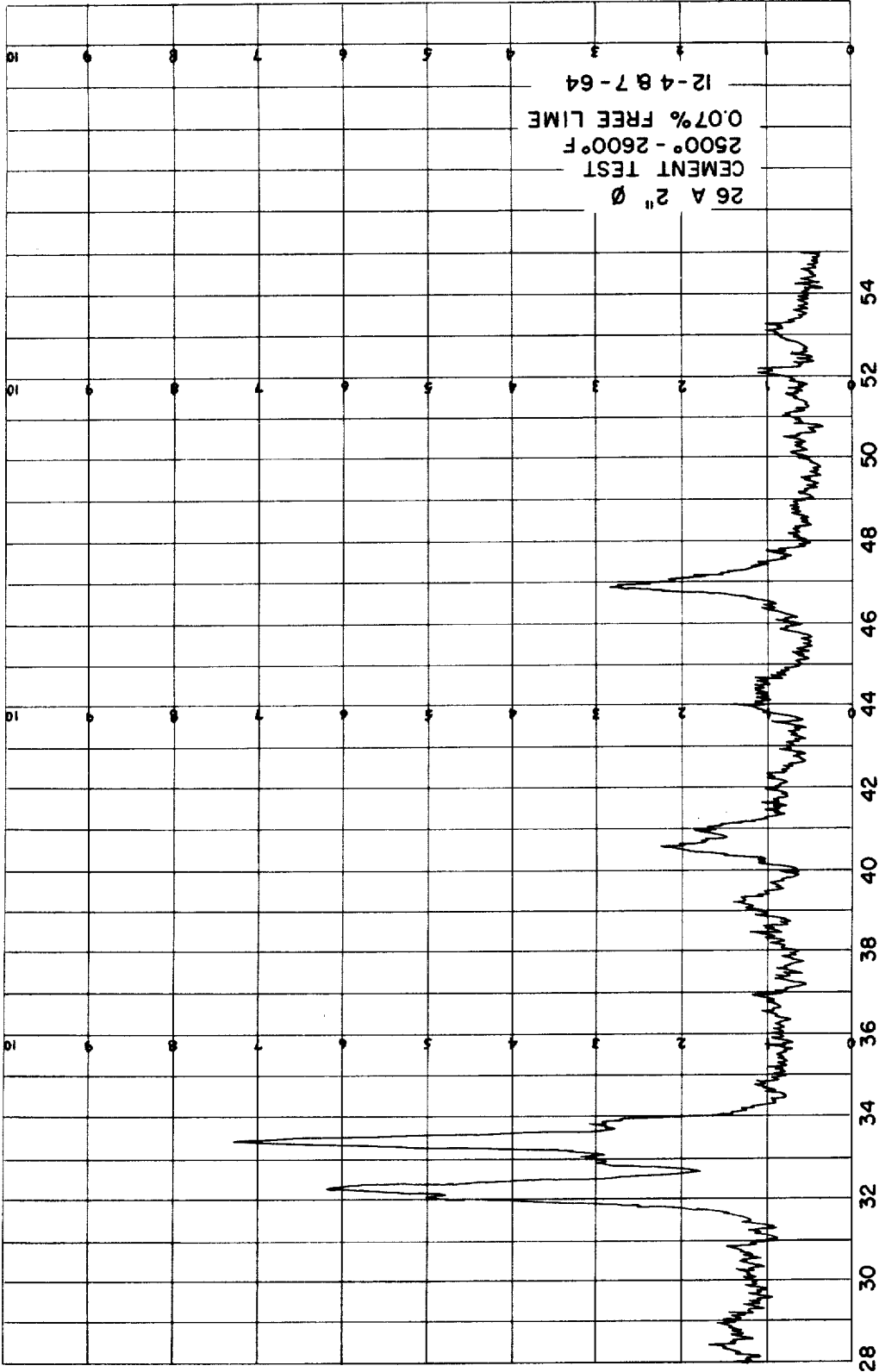


FIG. 4

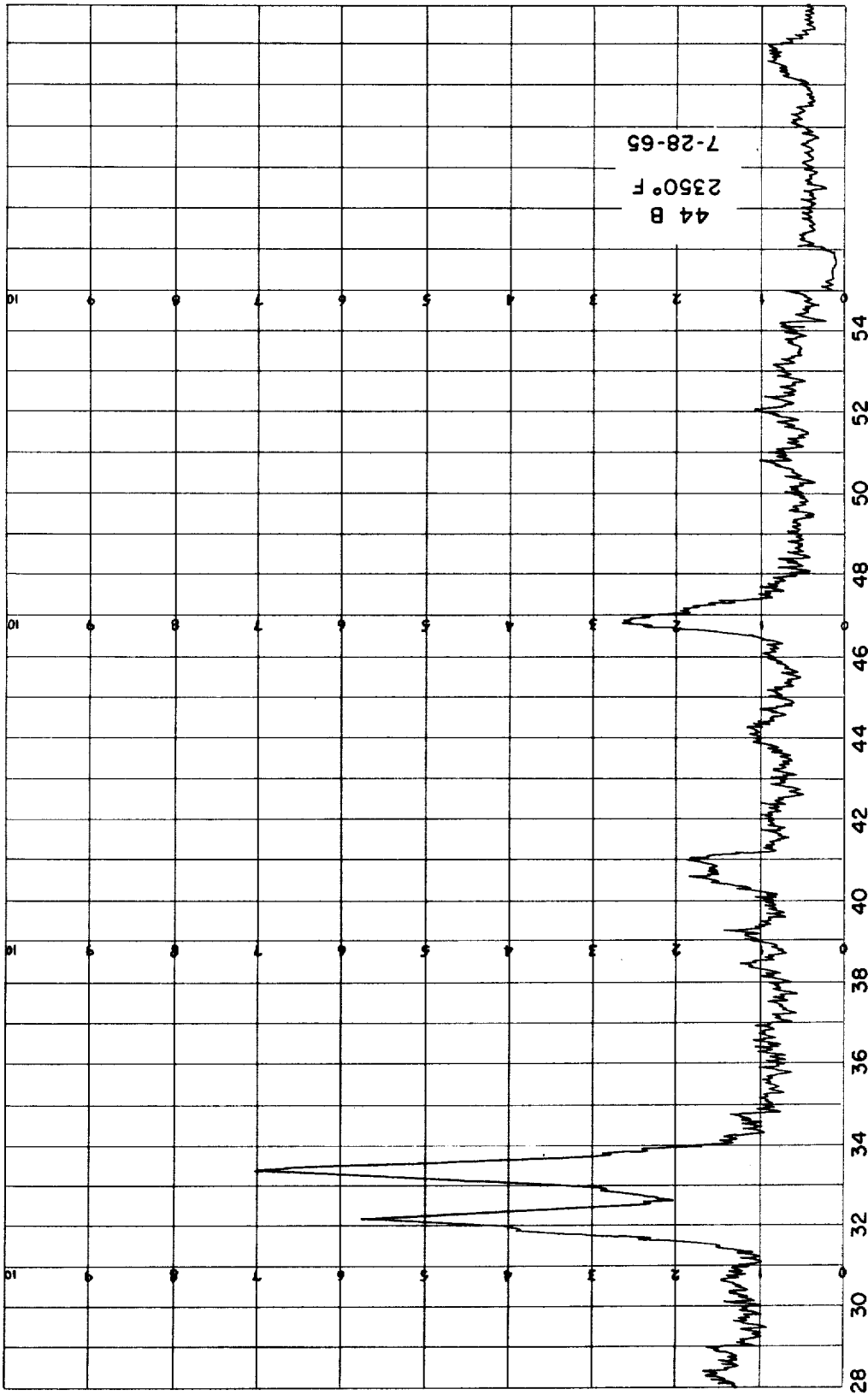


FIG. 5

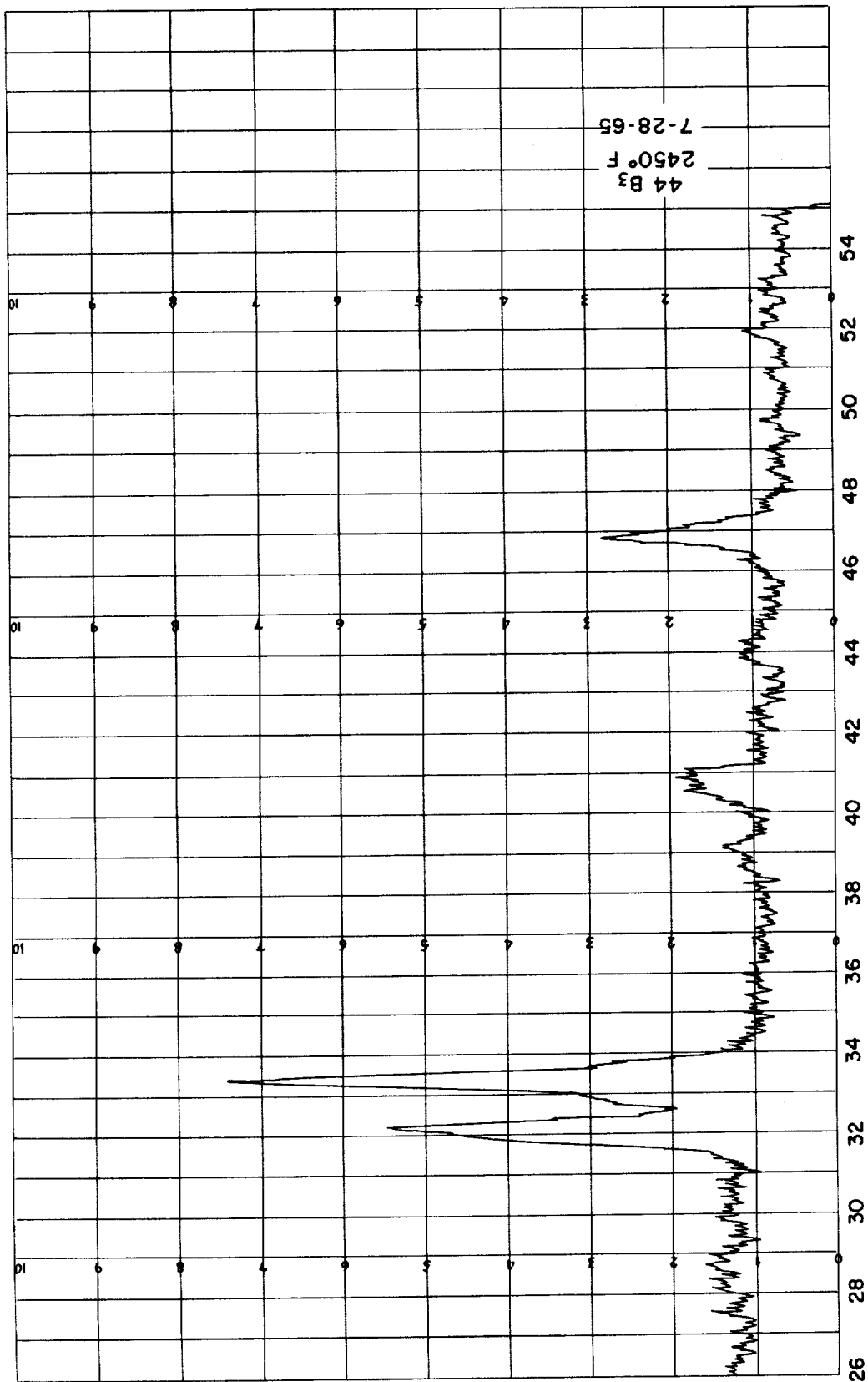


FIG. 6

HYDRAULIC CEMENT AND METHOD OF PRODUCING SAME

Matter enclosed in heavy brackets [] appears in the original patent but forms no part of this reissue specification; matter printed in italics indicates the additions made by reissue.

This application is a reissue of application Ser. No. 277,969 now U.S. Patent No. 3,861,928 which is a continuation-in-part of our copending application Ser. No. 85,776 filed Oct. 30, 1970, now U.S. Pat. No. 3,682,669, which was a continuation-in-part of application Ser. No. 70,596 filed Sept. 8, 1970 under Commissioner's Order 824 O.G. 1, which in turn was a continuation of parent application Ser. No. 652,275 filed July 10, 1976, the latter two being now abandoned.

The field of art to which the present invention pertains is the making of Portland-type cement.

The invention relates particularly to Portland-type cement and production thereof, and provides a method that, inter alia, results in a substantial savings in fuel and other operating costs and yields Portland-type cement that form products of substantially higher than normal compressive strengths.

In the conventional commercial practice for producing Portland cement, certain proportions of crushed calcium carbonate, aluminum oxide, silicon dioxide and ferric oxide are pulverized, either in dry or slurry form. The ground mixture is burned in a kiln, usually of the rotary type, to form solid "clinker" that is pulverized with a small amount of gypsum to form the cement.

It is well recognized in the art that the operation of the kiln for forming clinker accounts for one of the largest single elements in the cost of producing Portland cement.

The ground mixture must be burned at a temperature sufficiently high both to promote reaction in the solid state and to bring about fusion of the components, and thus to form clinker. The clinker is composed of calcium silicates, calcium aluminates, and calcium aluminoferrites, which constitute the hydraulically settable ingredients of cement formed by grinding the clinker.

Theoretically, the incipient fusion leading to the formation of the above-mentioned compounds can occur at a temperature of about 1338° C. (2440° F.). The formation of clinker is influenced by the amount of liquid formed in the fusion, which is governed by the amount of aluminum oxide and iron oxide in the ground mixture.

In the actual commercial operation utilizing rotary kilns at practical production rates, the residence or retention time of the material in the kiln at the above-mentioned minimum theoretical temperature is not long enough for the complete reactions to take place. Thus higher temperatures must be used to accelerate and complete the reactions between the components of the mix.

As indicated, for example, in the patents to Case, U.S. Pat. Nos. 2,004,463 of June 11, 1935, to Dyckerhoff, 2,970,925 of Feb. 7, 1961, and to Schifferle, 3,066,031 of Nov. 27, 1962, kiln temperatures of 1400° C. to 1450° C. (2550° F. to 2650° F.) are commonly utilized in commercial operations for forming cement clinker, although currently higher temperatures are usually used.

It is also well recognized in the prior art that the clinker produced by present commercial operations is

difficult to grind into a powder suitable for use as cement.

Stated in general terms, the present invention makes possible the production of Portland-type cement clinker at temperatures substantially lower than those presently employed in commercial practice, and clinker that is more readily grindable than clinker produced in present commercial operations. Furthermore, the resultant ground cement forms concrete and other cementitious compositions that possess compressive strengths superior to those exhibited by Portland cement as presently commercially produced.

The foregoing objects and advantages of the invention are achieved by incorporating into the ground mix of ingredients conventionally employed for the production of Portland cement, namely, limestone, silica, alumina and iron oxide, a relatively small portion of an additive material consisting essentially of a boron-containing component, and burning the mixture thus formed in a conventional Portland cement kiln.

It has been found that the inclusion of such an additive as a component of the mix makes possible the formation of cement clinker at temperatures of about 2350° F. to about 2550° F. at about the same kiln retention time as in conventional processes. Clinker produced in this manner has improved grindability characteristics as indicated, for example, by less energy being needed to grind the clinker to a given surface area. The compressive strength of Portland-type cement produced as described herein is substantially higher than the compressive strength of cement made from the same components but without the boron-containing component.

The curve of the accompanying drawing, FIG. 1, shows the relationship between the kiln burning temperature and the amount of free lime in clinker made in accordance with this invention.

To produce Portland-type cement according to this invention, there is first formed by conventional procedures a pulverized mixture of raw materials composed of minerals containing calcium oxide, silicon dioxide, aluminum oxide and iron oxide. Limestone can be utilized as the source of calcium oxide. Silicon dioxide can be supplied in the form of sand, clay or shale, which can also be the source of aluminum oxide. The source of iron oxide can be mill scale, a by-product of steel mills, pyrite cinders, a by-product of sulfuric acid production, or iron ore. Iron oxide also is usually present in the raw materials used as the source of silicon dioxide and aluminum oxide. The raw materials are carefully proportioned and blended to maintain the relative proportions of the oxides within certain desired limits, in accordance with well-known practice, to produce cement having desired properties and characteristics. Typically, a Portland cement has about 60 percent to 70 percent of lime as CaO, about 20 percent to 25 percent of silicate as SiO₂, about 2 percent to 6 percent of iron oxide as Fe₂O₃, and about 3 percent to 8 percent of alumina as Al₂O₃.

The pulverized mixture of the raw materials normally requires a burning temperature of the order of 2750° F. in the kiln to be transformed into a cement clinker composed of desired percentage amounts of calcium silicate, calcium aluminate and calcium aluminoferrite reaction products. In accordance with the present invention, however, a cement clinker containing the above-mentioned reaction products is formed at substantially lower burning temperatures in the kiln, namely, at temperatures of about 2350° F. to about 2550° F. This is

achieved by incorporating a relatively small amount of a boron-containing material into the pulverized mixture of the raw materials fed to the kiln.

The boron-containing additive is intimately blended and intermixed with the raw pulverized mixture, or can be interground in the initial grinding process, and the material thus blended is fed to the kiln for burning into clinker.

The presence of the boron-containing component in the raw material fed into the kiln enables the raw material to be transformed into a highly satisfactory clinker at temperatures substantially lower than those normally required for mixtures without the boron-containing additive. Moreover, the resultant clinker possesses improved grindability and yields a pulverized cement that forms concrete and other cementitious compositions having superior compressive strengths.

During burning of the conventional mixture, the rate and degree of completion of formation of the calcium silicate and calcium aluminate reaction products, particularly tricalcium silicate, is indicated by the amount of uncombined calcium oxide (CaO), so-called "free lime," present in the clinker. If the amount of free lime in the clinker exceeds about 2 percent by weight, the resultant cement might be unsatisfactory, particularly in that such cement is susceptible to excessive expansion.

By including the boron-containing additive in the raw materials fed to the kiln, the clinker not only is formed at temperatures that are substantially below those conventionally required, but does not contain undesired amounts of free lime. Clinker having a satisfactory free lime content of about 2 percent or less can be obtained at kiln temperatures in the range of about 2350° F. to about 2550° F. At kiln temperatures below that range, undesired amounts of free lime tend to be present in the clinker; at kiln temperatures above that range, the clinker might contain an undesired amount of free lime.

The composition of cement clinker produced according to this invention is different from that of conventional Portland cements. The hydraulically settable calcium silicates in ordinary Portland cements are tricalcium silicate, called Alite and referred to as C₃S, and the beta form of dicalcium silicate, called Belite and referred to as C₂S. By weight of the clinker, the tricalcium silicate is typically present in an amount of about 30 percent to 35 percent in Type IV to about 60 percent to 65 percent in Type III, and the beta-dicalcium silicate is typically present in an amount of about 40 percent to 45 percent in Type IV to about 15 percent to 25 percent in Type III. Together, these two constituents normally comprise about 70 percent to about 85 percent of the clinker in all of Types I to V Portland cement.

Cement according to this invention, on the other hand, is characterized by the presence of dicalcium silicate in its alpha-prime form, which can be referred to as α'-C₂S, and also by the presence of borate which appears to be dissolved with lime in the α'-C₂S silicate phase of the clinker in a ratio of five mols of CaO per mol of B₂O₃. α'-C₂S can be present in varying amounts and should be the major constituent of the clinker. From raw materials ordinarily used to make Portland cement the α'-C₂S preferably is present in an amount of about 65 percent to about 85 percent by weight. The amounts of potential C₃S and beta-C₂S compounds that would otherwise form are reduced, and usually appear to be present in such small amounts, if at all, that they cannot readily be identified by x-ray diffraction.

With the foregoing differences in mind, the Bogue equations can be used to compute potential clinker compound composition from oxide analysis of the raw feed mix. Tetracalcium aluminoferrite (C₄AF) and tricalcium aluminate (C₃A) are calculated as usual. α'-C₂S is calculated on the total silicate content, and the borate is calculated at a ratio of 5 mols of CaO per the lime requirement for mol of B₂O₃. Zero tricalcium silicate (C₂S) is assumed in the calculation. The lime content of the raw mix preferably should be about 0.5 percent in excess of theoretical for complete formation of the potential clinker compounds.

The boron-containing additive used in the practice of this invention is an oxide of boron, a compound containing an oxide of boron or a compound that yields an oxide of boron at the temperatures prevailing in a cement kiln. Examples of such boron-containing additives are boric acid anhydride, acids of boric acid anhydride, salts of boric acid anhydride, polyboric acids and polyborates such as diborates, triborates and tetraborates of ammonium, sodium, potassium, calcium, barium, strontium and magnesium, and boron-containing refined and unrefined minerals or ores, including colemanite, ulexite, danburite, pinnoite, ascherite and rasilite. Boron trioxide (B₂O₃), raw colemanite and refined colemanite are preferred. The quantity of the boron-containing additives incorporated in the pulverized mixture of raw ingredients fed to the kiln relatively small. An amount sufficient to provide a B₂O₃ content in the range of about 1 percent to about 3 percent by weight of the pulverized mixture, preferably about 1.5 percent to about 2.5 percent, should be used, which amounts approximately can then be found in the clinker.

In an actual embodiment of the invention, a modified typical Type II Portland cement pulverized mix was made up with the following components:

Cataract Limestone	[72.58%]	[72.39%]	72.39
Cataract Shale	[16.60]	[16.56]	16.56
Winship Clay	[3.67]	[3.66]	3.66
Pyrite Cinders	[2.39]	[2.38]	2.38
Special Additive No. 1	[4.76]	[5.00]	5.00
"A Modified"	[100.00%]	[99.99%]	99.99%

Special Additive No. 1 contained:

SiO ₂	8.00%	Na ₂ O	5.19%
Fe ₂ O ₃	0.19	K ₂ O	0.23
Al ₂ O ₃	0.35	B ₂ O ₃	36.13
CaO	14.66	Ign. Loss	32.57
MgO	2.67	Total	99.99%

Thus, the mix had the following calculated composition:

SiO ₂	22.55%
Al ₂ O ₃	5.82
Fe ₂ O ₃	4.45
CaO	64.85
B ₂ O ₃	1.86
	99.53%

Batches of the foregoing A. Modified mix were burned at various temperatures for a period of time equal to a typical Portland cement kiln retention time at normal operation temperature of about 2800° F. The

clinker prepared from each such batch contained the following amount of free lime *by titration analysis*;

Burn Temperature °F.	% Free Lime
2150	11.11
2250	4.24
2350	1.76
2450	0.77
2550	1.98
2650	2.26
2750	1.60
2850	1.27

The curve of the accompanying drawing, FIG. 1, is based on the above-tabulated data, and clearly shows that clinker having a desirably low level of free lime can be prepared at burn temperatures in the range of about 2350° F. to about 2550° F., a range of temperature markedly lower than the temperatures usually employed to make Portland cement clinker having satisfactory low free lime content.

The production of a satisfactory cement clinker thus is possible at reduced kiln temperatures, and substantial savings in fuel cost as well as other benefits can be obtained. Fuel savings that amount to the order of about 300,000 BTU per barrel of cement clinker produced have been calculated. Also, by virtue of the lower temperatures utilized in the kiln operation, longer kiln shell life and less frequent replacement of the refractory lining of the kiln are benefits that result in substantially reduced kiln maintenance cost. This cost reduction has been estimated to be in the order of about 10 percent.

In addition to and perhaps even more important than the foregoing advantages accruing from the use of the described boron-containing additives in accordance with this invention is the improvement thereby obtained with respect to the compressive strength of the resultant cement. Indicative of the superior strength characteristics of Portland-type cement made from clinker produced in accordance with the invention are the data set forth hereinbelow.

As a control, a typical Type II Portland cement mix without modification by an additive component of this invention was burned at about 2800° F. for about 30 minutes. The mix had the following raw materials and calculated compositions:

Cataract Limestone	76.21%
Cataract Shale	17.43
Winship Clay	3.85
Pyrite Cinders	2.51
"A. Control"	100.00%
SiO ₂	22.50%
Al ₂ O ₃	5.89
Fe ₂ O ₃	4.52
CaO	65.17
	98.08%

The free lime content of the clinker was 0.72 percent *by titration analysis*.

Compressive strength tests (ASTM Test C 109-64) were conducted on mortar cubes 2 inches×2 inches×2 inches made of the A. Control cement described above and the A. Modified cement according to this invention from clinker burned at 2450° F. The cubes were kept in a cabinet in which the atmosphere was controlled at 70° F. and 100 percent relative humidity. The compressive strength of the cubes was tested after 7 and 28 days. The following table presents the results obtained and

various factors involved in making the tests for the cements described above and also for another cement according to this invention ("B. Modified") to be described:

	A. Modified	A. Control	B. Modified
Clinkered Temp. (°F.)	2450	2800	2550
B ₂ O ₃	1.86	—	1.54
Free Lime (%)	0.77	0.72	2.17
Blaine Fineness	3591	4195	3585
SO ₃ Added (%)*	1.52	1.94	0.59
Water (cc.)	230	250	230
Initial Set (hr.:min)	4:20	1:10	2:30
Final Set (hr.:min.)	7:00	3:40	7+
Compressive Strength:			
7 days (psi)	4558	3133	4308
28 days (psi)	9375	5267	9258

*As gypsum to make cement.

The B. Modified cement was prepared from a raw material mix containing 95.24 parts by weight of the A. Control cement raw material mix and 4.76 of Special Additive No. 1 A (typical B₂O₃ content of 32.40 percent) and had a calculated composition as follows:

SiO ₂	21.40%	B ₂ O ₃	1.54%
Fe ₂ O ₃	4.30	Na ₂ O	0.26
Al ₂ O ₃	5.60	Insol.	0.82
CaO	63.57	H ₂ O	0.82
		Total	98.31%

Clinker was formed by burning the raw mix at 2550° F. for about 30 minutes, and had a free lime content of about 2.17 percent *by titration analysis*.

Compressive strength tests of steam-cured mortar cubes were made using a cement modified according to this invention ("C. Modified") and an unmodified typical Type II pipe cement as a control ("B. Control").

The C. Modified cement was made from clinker formed at a burning temperature of about 2650° F. for about 30 minutes from a raw mix of [6.79] 7.28 parts of Special Additive No. 2 (unrefined Kern County colemanite containing [34.11] 24.73 percent B₂O₃) and [93.21] 92.72 parts of the B Control mix. The [clinker from this] raw mix had a calculated [analysis] loss free composition of:

SiO ₂	22.63%
Al ₂ O ₃	5.71
Fe ₂ O ₃	4.37
CaO	64.79
B ₂ O ₃	1.87
"C. Modified"	99.37%

The clinker had a free lime content of about 1.93 percent, *by titration analysis*.

As a control cement, the B. Control mix was burned at 2800° F., about 1.48 percent free lime, ground and used. The B. Control cement had an analyzed composition as follows:

SiO ₂	21.96%
Fe ₂ O ₃	3.28
Al ₂ O ₃	4.80
CaO	64.87
SO ₃ =	2.38

-continued

"B. Control"	97.29%
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*Added as about 5% gypsum.

Cubes were made from mortar containing 1982 grams of sand and 793 grams of the B. Control cement and the C. Modified cement, and were cured for 20 hours in a cabinet maintained at 165° F. with steam. Thereafter, the cubes were placed in a cabinet at 70° F. and 100 percent relative humidity, and compressive strength tests were made on the cubes after 14 hours, 7 days and 28 days. The following tabulation sets forth the strengths and other factors associated with this test:

	C. Modified	B. Control
Flow Consistency (% H ₂ O)	38	41
Water Added (cc.)	300	325
Flow Reading	73.5	71.5
Blaine Fineness	3662	4014
Initial Set (hr.:min.)	—	2:30
Final Set (hr.:min)	7:00	4:25
Compressive Strength:		
14 hrs. (psi)	5350	5525
7 days (psi)	7438	6462
28 days (psi)	9300	7412

Compressive strength tests were also conducted on concrete cylinders (ASTM Test C192-65) made from a Type II Portland cement modified according to this invention ("D. Modified") and an unmodified Type II cement ("C. Control"). The clinker used to make the D. Modified cement had an analysis of:

SiO ₂	24.46%
Fe ₂ O ₃	3.96
Al ₂ O ₃	4.72
CaO	63.15
B ₂ O ₃	1.97
"D. Modified"	98.26%

and contained 1.60 percent free lime after burning at about 2500° F. in a kiln for a usual kiln retention time of about 30 minutes. The raw material mix contained about 2.0 percent of B₂O₃ supplied as boron trioxide. The C. Control cement, which contained 1.12 percent free lime, analyzed as:

SiO ₂	22.02%
Fe ₂ O ₃	3.60
Al ₂ O ₃	4.74
CaO	64.67
SO ₃ =	2.09
"C. Control"	97.12%

*Added as about 5% gypsum

Six sacks (94 lbs.) of each cement was mixed per cubic yard with 3/4 inch Neilsen (Calaveras County, Cal.) coarse aggregate and sufficient water to provide a 4 inch slump. Cylinders 6 inches in diameter and 12 inches long were cast with the concrete and kept at 70° F. and 100 percent relative humidity. The cylinders had the following strengths:

	C. Control	D. Modified
7 days (psi)	2420	3080

-continued

	C. Control	D. Modified
14 days (psi)	3400	4375

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From the foregoing data based on compressive strength tests, it is evident that cements made with the boron-containing additives according to this invention have significantly greater strength, even though made at markedly lower kiln burning temperatures, than Type II Portland cements.

To determine the nature of the compounds in the clinker made according to the instant invention, various samples of clinker made as described herein were subjected to x-ray diffraction analysis. For comparison, a commercial Type II Portland cement was also analyzed; it had the following content:

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SiO ₂	22.94
Fe ₂ O ₃	3.47
Al ₂ O ₃	4.95
CaO	66.93
"C. Control"	98.29

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FIG. 2 shows the pertinent section of the x-ray diffraction chart of the analysis, from which can readily be seen the characteristic peaks at angle 2-theta of 29.3° for C₂S, 34.3° for beta-C₂S, 32.2° and 32.6° for both C₂S and beta-C₂S, 33.2° for C₃A and 33.8° for C₄AF. The distinct appearance of these values is characteristic of all of Types I to V Portland cement.

By contrast, FIGS. 3, 4, 5 and 6 show characteristic peaks at 32.4° and 33.2° for α-C₂S, 33.2° also for C₂A and 33.8° for C₄AF, but no discernible values at 29.3 for C₂S or at 34.3° for beta-C₂S.

FIG. 3 is based on analysis of the D. Modified clinker described previously herein.

FIG. 4 is the analysis of clinker burned at 2550° F., free lime of 0.07 percent, that contained in the raw mix 3.29 percent B₂O₃ from 9.09 percent of Special Additive No. 1A. Cement made with this clinker and 3.74 percent gypsum had the following analysis:

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SiO ₂	24.44%
Fe ₂ O ₃	2.93
Al ₂ O ₃	4.59
CaO	59.78
B ₂ O ₃	Not determined
SO ₃	2.20
Na ₂ O	0.54
K ₂ O	0.32
	94.80%

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FIGS. 5 and 6 show the x-ray diffraction analysis of clinker made from raw mix containing 97 parts having the following composition:

SiO ₂	23.06%
Fe ₂ O ₃	3.28
Al ₂ O ₃	4.92
CaO	67.60
	98.86%

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and 3 parts of boric acid anhydride. The clinker of FIG. 5 was burned at 2350° F. and that of FIG. 6 at 2450° F.; the free limes were 1.76 percent and 1.05 percent, respectively, by titration analysis.

It has also been found, quite surprisingly, that cement clinker produced in accordance with the invention is more readily grindable than is clinker as normally produced, i.e., without inclusion of the boron-containing component in the mix. Tests indicative of the grindability of the instant clinker as compared with clinker as normally produced were conducted in jar mills following procedures commonly accepted in the art, namely, by determining the Blaine surface area of the ground clinker at various stages of grinding. In specific terms, actual tests have shown that, by virtue of the improved grindability of clinker embodying this invention, production of the ground cement from such clinker can be increased approximately 140 percent to 200 percent.

For example, one cement made from clinker embodying this invention had a Blaine surface area of 3600 sq. cm. per gram after 4080 revolutions of a jar mill, whereas a comparable clinker as normally produced required 6120 revolutions to produce cement of substantially the same Blaine surface area (3590 sq. cm. per gram).

In another grindability test, the clinker of the D. Modified cement described above and a clinker corresponding thereto but produced without a boron-containing additive were ground. The latter clinker had the following analyzed composition:

SiO ₂	23.52%
Fe ₂ O ₃	3.72
Al ₂ O ₃	4.70
CaO	66.46
Free Lime	0.92
"D. Control"	99.32%

3,000 grams of each clinker were ground with 3.5 cc. of Zeemill grinding aid, 6.0 cc. of water and 90 grams of gypsum for the D. Control and 71 grams of gypsum for the D. Modified. To achieve a Blaine surface area of about 4,000 sq. cm. per gram, a fineness to which pipe cement is commonly ground, the D. Modified clinker required about 10,700 revolutions of the mill whereas the D. Control clinker required about 22,900 revolutions.

These grinding data demonstrate the remarkably improved grindability of clinker made in accordance with this invention.

It will be apparent to persons skilled in the art that numerous changes can be made in the ingredients, conditions and proportions set forth in the foregoing illustrative embodiments without departing from the invention as described herein before and as defined in the appended claims.

We claim:

1. A hydraulic cement composition containing alpha-prime dicalcium silicate as a hydraulically settable calcium silicate in an amount by weight of about 65 percent to about 85 percent of said composition and borate.

2. A hydraulic cement composition according to claim 1 substantially free from tricalcium silicate and from beta dicalcium silicate.

3. A hydraulic cement composition according to claim 1 wherein the amount of free lime is less than about 2 percent by weight of said composition.

4. A hydraulic cement composition according to claim 1 further containing borates present in a 5:1, lime to boric oxide ratio on a molar basis.

5. A hydraulic cement composition according to claim 4 wherein said borate calculated as B₂O₃ is about

1 percent to about 3 percent by weight of said composition.

6. A hydraulic cement composition according to claim 5 wherein said borate is in solid solution in said alpha-prime dicalcium silicate.

7. A hydraulic cement composition according to claim 5 wherein said borate is B₂O₃ in solid solution in said alpha-prime dicalcium silicate.

8. A Portland-type cement composition containing alpha-prime dicalcium silicate as a hydraulically settable calcium silicate in an amount by weight greater than the amount by weight of any other constituent in said composition.

9. A Portland-type cement composition according to claim 8 wherein said alpha-prime dicalcium silicate is about 65 percent to about 85 percent by weight of said composition.

10. A Portland-type cement composition according to claim 8 substantially free from tricalcium silicate and from beta dicalcium silicate.

11. A Portland-type cement composition according to claim 8 wherein the amount of free lime is less than about 2 percent by weight of said composition.

12. A Portland-type cement composition according to claim 8 further containing borate, present in a 5:1, lime to boric oxide ratio on a molar basis.

13. A Portland-type cement composition according to claim 12 wherein said borate calculated as B₂O₃ is about 1 percent to about 3 percent by weight of said composition.

14. A Portland-type cement composition according to claim 13 wherein said borate is in solid solution in said alpha-prime dicalcium silicate.

15. A Portland-type cement composition according to claim 13 wherein said borate is B₂O₃ in solid solution in said alpha-prime dicalcium silicate.

16. A hydraulic cement composition containing tricalcium aluminate, tetracalcium aluminoferrite and alpha-prime dicalcium silicate as hydraulically settable components and borate and being substantially free from tricalcium silicate, and wherein said alpha-prime dicalcium silicate is present in an amount by weight greater than the amount by weight of either said aluminate or aluminoferrite.

17. A hydraulic cement composition according to claim 16 wherein said alpha-prime dicalcium silicate is about 65 percent to about 85 percent by weight of said composition.

18. A hydraulic cement composition according to claim 16 substantially free from beta dicalcium silicate.

19. A hydraulic cement composition according to claim 16 wherein the amount of free lime is less than about 2 percent by weight of said composition.

20. A hydraulic cement composition according to claim 16 further containing borate present in a 5:1, lime to boric oxide ratio on a molar basis.

21. A hydraulic cement composition according to claim 20 wherein said borate calculated as B₂O₃ is about 1 percent to about 3 percent by weight of said composition.

22. A hydraulic cement composition according to claim 21 wherein said borate is in solid solution in said alpha-prime dicalcium silicate.

23. A hydraulic cement composition according to claim 21 wherein said borate is B₂O₃ in solid solution in said alpha-prime dicalcium silicate.

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24. A method of making a Portland-type hydraulic cement that contains alpha-prime dicalcium silicate as a hydraulically settable calcium silicate which comprises forming an admixture of pulverized lime-containing material, silicon oxide-containing material, aluminum oxide-containing material, iron oxide-containing material and a boron-containing substance sufficient to provide at least about 1% by weight of B₂O₃ in said admixture, proportioning the amounts of said materials in said admixture stoichiometrically on the basis of potential tricalcium aluminate, tetracalcium aluminoferrite and alpha-prime dicalcium silicate compounds and borate at a ratio of five mols of calcium oxide per mol of B₂O₃, heating said admixture to fuse the components thereof into clinker and to form said alpha-prime dicalcium silicate in an amount greater than the amount of any other constituent, and grinding said clinker.

25. A method according to claim 24 wherein said boron-containing substance is an oxide of boron, a compound containing an oxide of boron or a compound that yields an oxide of boron at the temperatures prevailing in a cement kiln.

26. A method according to claim 24 wherein said boron-containing substance is boric acid anhydride, an acid of boric acid anhydride, a salt of boric acid anhy-

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dride, a polyboric acid, a polyborate of ammonium, sodium, potassium, calcium, barium, strontium or magnesium, a boron-containing mineral or a boron-containing ore.

27. A method according to claim 24 wherein said boron-containing substance is boron trioxide, raw colemanite or refined colemanite.

28. A method according to claim 24 wherein the amount of said boron-containing substance as B₂O₃ is in the range of about 1 percent to about 3 percent.

29. A method according to claim 24 wherein said pulverized materials are limestone, silica, alumina and iron oxide.

30. A method according to claim 24 wherein said admixture is heated at above about 2350° F.

31. A method according to claim 24 wherein said admixture is heated at below about 2750° F.

32. A method according to claim 24 wherein said admixture is heated at between about 2350° F. and about 2550° F.

33. *A method according to claim 24 wherein the lime content of the admixture prior to heating is about 0.5 percent in excess of theoretical.*

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UNITED STATES PATENT AND TRADEMARK OFFICE
CERTIFICATE OF CORRECTION

PATENT NO. : Re. 31,118
DATED : Jan. 4, 1983
INVENTOR(S) : Slater, deceased, et al.

It is certified that error appears in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

First page, 2nd col., line 8, "Slatter" should read --Slater--. Col. 1, line 17, "1976" should read --1967--; line 67, "It" should read --[It--. Col. 2, line 2, "-ment" should read --ment.]--; line 6, ", and" should read --. [and--; line 8, "operations." should read --operations.]--; line 25, "Clinker" should read --[Clinker--; line 28, "area." should read --area.]--. Col. 3, line 14, "possesses" should read --[possesses--; line 15, "and" should read --and]--. Col. 4, line 6, after "and" insert --the lime requirement for--; lines 7-8, delete "the lime requirement for"; line 29, after "kiln" insert --is--; lines 41-44, delete the entire second column of figures including the heavy brackets. Col. 6, lines 24 and 25, "B₂O₃ content of 32.40 percent)" should be italicized. Col. 9, line 1, "It" should read --[It--; line 46, "invention." should read --invention.]--; line 68, "B₂O₂" should read --B₂O₃--.

Signed and Sealed this

Fourteenth Day of August 1984

[SEAL]

Attest:

GERALD J. MOSSINGHOFF

Attesting Officer

Commissioner of Patents and Trademarks