Portland cement and method of retarding the setting rate thereof

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ABSTRACT available in

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DESCRIPTION (OCR text may contain errors)

CLAIMS available in

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COATING R PLAS'HC Patented Apr. 24, 1945 Examiner PORTLAND CEMENT AND METHOD OF RE- TABDING THE SETTING RATE THEREOF Myron A. Swayze, Hudson, N. Y., assignor to Lone Star Cement Corporation, New York, N. Y., a

corporation of Maine No Drawing. Application May 14, 1940, Serial No. 335,139

7 Claims.

This invention relates to Portland and Portland type cements with a retarded setting rate, and to methods of retarding the rate of setting of such cements at elevated temperatures. More particularly, the invention concerns a 31313910- ting cement and method of retarding the set ting rate of cements for use in 3 11 wells.

In the cementing of oil wells and similar operations, it is usual to mix Portland cement with about 40 to 50% of water, by weight, to introduce this grout or slurry into the well casing, and to pump it to the place where it is desired to harden. This practice can be carried out readily in wells that are not very deep, but in the deeper wells such as those 6,000 to 12,000 feet or more in depth, longer periods of time are required for pumping the grout into position and high temperatures are encountered accelerating the setting of the cement, so that grouts made with ordinary Portland cement frequently become too stifi' for pumping and set before they reach their ultimate location.

Ordinary Portland cement when mixed with water to form a paste sets much faster at elevated temperatures than it does at normal tem peratures, because at the higher temperatures hydration begins immediately and the paste is stiffened sufiiciently to prevent easy deformation in a very short time. This dimculty in pumping ordinary cement grouts is aggravated in oil wells because during the passage of the grout down through an oil well casing and then upward around the lower end of the casing to the position where it is to harden, the grout is required to pass through narrow channels, making pumping virtually impossible if premature stififening has taken place.

various Portland cements and means for overcoming these dimculties have been proposed with more or less success. To be entirely satisfactory for use in cementing deep oil wells, however, a cement should have the property when mixed with water of remaining pumpable for long periods of time at elevated temperatures, and should be of sufiicient fineness to remain uniformly suspended in the water until the grout has reached its final destination and has started to set. The fineness oi the cement has an important efiect on the setting rate of the grout, because the finer a cement is ground, the more reactive surface is exposed and the faster is the setting rate of the grout made with the cement. It is particularly diihcult, therefore, to provide Portland cements of sufiicient fineness toprevent settling out that also have a sufiiciently slow setting rate to make practical their use in deep oil wells,

Various retarders have been proposed for admixture with Portland cement to retard the rate of setting of the grout. Some of these retarders, however, have been required in rather large amounts in order to produce a sufiiciently slow setting rate, and as a consequence the presence of the retarding agent may have some detrimental efiect on the ultimate strength of the hardened cement. Other retarders produce some other objectionable result although delaying substantially the initial setting of the cement.

It is an object of my invention to provide a Portland or Portland t of cement to which only a small proportion o; a very eflective setting rate retarder has been added. so that a grout made with this cement has a greatly prolonged setting rate and after hardening has a high strength.

Another object of my invention is to retard the setting rate of Portland cement, even though it is ground very fine, by he addition of a small proportion of a dextrinsiba starch Another objec promon 0 Por land cement containing small proportions of dextrin and a starch containing fiour whereby the cement has a s ow re 0 se mg at high temperatures, does not settle out when mixed with water and has a high strength after hardening.

A further object is the provision of methods of preparing and using Portland cements having the foregoing roperties.

I have found that a dextrin or starch, or both, i when added in very small amounts to Portland cements, has an unusually strong retarding ef- 3 i'ect on the rate of setting of such cements at elevated temperatures up to and even above 200 F. Dextrin is generally considered to be an intermediate product in the hydrolysis of starch to sugars such as dextrose or maltose, and any of the commercial dextrins may be employed in accordance with my invention. The dextrin may be derived, for example, fmg subjection of various kinds of starch, including corn starch, potato starch, cassava starch and my Bea! morder 0 0 0., or the dextrin may be prepared by heating various starches with acids or diastase at high or low temperatures. I preier E employ" a dextrin which has a high adhesive power and which does not contain too large a proportion of sugar. -For this reason, the dextrins prepared by the action of dry heat are preferable.

The starches that are suitable for purposes of this invention are the soluble starches that form stiff gels with water. owroot ch has been found to be very sa actory or purpose. These dextrins or starches may be used alone or in various combinations with each other, the particular proportions of the ingredients when used in combination not being critical.

A good grade of dextrin is very effective in slowing down the setting rate of Portland cement mixed with water to form a grout, appreciable effects being obtained with as little as 0.02% of dextrin by weight based on the weight of the dry cement. For ordinary purposes, I prefer to employ about 0.1% of dextrin or starch when this is used alone as a retarding agent. although the best proportion to use will depend to some extent on the composition of the particular Portland cement to which it is added. and upon the fineness of this cement, as well as upon the amount of retarding effect that is needed.

Dextrin, employed alone as a retarding agent for Portland cement has a tendency to cause the cement to settle out from a water slurry of the cement. Unless the cement employed is extremely fine or only a very small proportion of dextrin is added, therefore, I prefer to employ a mixture of d grm with starch gas suitable starch containing e mix e of these other materials with dextrin provides a retarding agent that has the desired retarding effect on the setting rate of the Portland cement to a marked degree and that does not hasten the settling out of the cement or substantially impair the ultimate strength of the hardened cement.

The various flours that may be used in conjunction with dextrin include the in iiours such as wheat corn and go flour, and also other vegetable flours including otato, so Ean t flour and the like. Any he starch containing flours in general may be used for this purpose. Considerable variation in the proportions of dextrin and flour are possible with different cements.

I have found that a particularly satisfactory setting rate retarder for high grade Portland cements consists of 0.1% by weight of a mixture of equal parts dextrin and flour, or in other words. 0.05% of dextrin and 0.05% of flour. Such a small amount of retarding agent has a negligible effect on the ultimate strength of the cement. but permits the grout of the cement to be pumped easily into the desired location in a deep of the cement mente area afte hardened.

In order to illustrate the eflectiveness of the retarding agents of thi invention on the rate of setting of Portland cements, pumpability tests have been made with various commercial Portland cements, using a special apparatus known as the Halliburton consistometer" to determine the rate of setting of the cement at elevated temperatures. This apparatus is designed to simulate pumping conditions in an oil well at elevoted tem eratures and is described in U. 8. Patent No. 2,122,765. It consists essentially of a rotatin cylindrical container, with an internal addle assembly fixed to a head whose movement is independent of the container. With the container filled with cement slurry. the thrust against the paddle due to rotation of the container and the viscosity of the slurry is transferred from the head of the apparatus to a pendulum lever arm by a suitable connection. The pendulum range is graduated from 0 to 10 divisions, representing slurry viscosities of approximately 040,000 centipoises. A pull of 10 divisions on the pendulum is considered to represent the limit of pumpability for the slurry in an oil well. The temperature of the slurry during test is maintained at a constant high degree by a thermostatically controlled bath surrounding the container.

The following table indicates the effect of the retarding agents of my invention on the rate of setting and strength of two Portland cements of commercial manufacture. as determined by pumpability tests made in the Halliburton consistometer" at a temperature of 170 F. The column designated "Pumpability" is the time in minutes required for the viscosity of the paste to

reach a pull of 10 divisions in the consistometer." Strengths were determined by curing 2" cubes for 1 day, 3 days and '7 days at a temperature of 170 F.

TABLE I Eflect of retarders on properties of cement elm-r11 (40% water-411 tests at 170 F.)

PUMPABILITY Retarder Cement "A" Cementli" Minutes Minutes None 127 .10% arrowroot starch. 336 236 .05 extrin 276 171 .05% dextrin; .05% flour I 303 174 COMPRESSIVE STRENGTH Cement "A" Cement "B" 1 day adsys 7days 1 day 8 days 7days None 6.476 8,288 $.81? 6.925 8.4% 8.988 .10% snowroot starch 2.575 8,150 8,fl)0 6.062 8,625 9.212

.057 dextrin 5.275 8.060 8,912 7.550 10,080 10,150 dextrin; .05%

flour 5.825 8J1!) 8.150 7,525 9,425 10. 275

1 Standard brand of wheat flour.

The dextrin used in the foregoing tests was yellow technical form of corn dextrin purchased on the market. These tes cate the normal high ultimate strength of cements to which retarders have been added according to this invention, even though the early strength in the case of a starch addition is lowered somewhat.

The cements tested had the following composi- M tion.

Y7 Cement A" Cement 13" 22. 04 2a 09 a. so 4. as s. 10 4. s1 c4. 00 s5. 18 1.00 0. e2 1. 46 1. 04 o. as o. 52 99.86 99. 52 .oo 0. 0a 0.0 5. s .0 0.6 2. s 0 jange of (2,1 n o-a 0 DQ151888 square 0111. per gram 0 cement) l. 820 1, 800

In general, the proportion of retarding agent employed according to this invention should be about 0.02 to about 0.5% by weight of the dry cement. More than 0.5% of the retarding agent CUM OR PLASTIC serves no useful purpose and is uneconomical. Also, if too much retarding agent is employed, the setting rate may be actually increased and the ultimate strength of the hardened cement will be effected. An appreciable retarding effect is ob- .tained with amounts of dextrin or a starch, or both, as low as 0.02% and, for most practical purposes, it will be unnecessary to use more than 0.25% of these materials as retarding agents.

The retardin a in adryformwi such as during the grinding thereof man 8,0 ure,

oraftqrj, ground. If a dextrin is to be used as the retardifiiigent, starch may be ground with the cement at a temperature of around 200 C. to convert this starch to dex- Examiner retard the setting rate thereof at elevated temperatures which comprises distributing throughgut the dry cement amounts of dextrin up to about 3. Portland cement containing, as an agent to retard the setting rate of said cement at elevated aemperatures, dextrin in amounts up to about 4. Portland cement containing, as an agent to retard the setting rate of said cement at elevated temperatures, a water-soluble carbohydrate selected from the group which consists of dextrin and starches in amounts up to about 0.1%.

5. A method of preparing Portland cement to retard the setting rate thereof at elevated temperatures which comprises distributing through out the dry cement a water-soluble carbohydrate selected from the group consisting of dextrin and starches in amounts up to about 0.1%.

6. Portland cement containing, as an agent to retard the setting rate of said cement at elevated geinperatures, a starch in amounts up to about 7. A method of preparing Portland cement to retard the setting rate thereof at elevated temperatures which comprises distributing throughout the dry cement amounts of a starch up to about MYRON A. SWAYZE.

REFERENCED BY

Citing Patent	Filing date	Publication date	Applicant	Title
US2429211 *	Feb 7, 1944	Oct 21, 1947	Charles Ludwig Norman	High-temperature cement modifier
US2470505 *	Jun 28, 1946	May 17, 1949	Universal Atlas Cement Company	Slow setting cement and process of making the same
US2471632 *	Feb 12, 1947	May 31, 1949	Universal Atlas Cement Company	Retarded cement
US2489793 *	Jan 23, 1947	Nov 29, 1949	Universal Atlas Cement Company	Low water loss cement containing pregelatinized starch
US2576955 *	Oct 18, 1946	Dec 4, 1951	Universal Atlas Cement Company	Low-water-loss cement
US2619181 *	Jul 11, 1949	Nov 25, 1952	Phillips Petroleum Co	Low water-loss cement slurry
US2655004 *	Feb 25, 1946	Oct 13, 1953	Wertz Louis S	Composition for and method of solidifying porous masses and structures
US2662827 *	Mar 12, 1946	Dec 15, 1953	Stanolind Oil & Gas Co	Well cementing
US2823135 *	Jan 6, 1956	Feb 11, 1958	Toulmin Jr Harry A	Low water loss cement slurry comprising dextran
US2833660 *	Dec 31, 1952	May 6, 1958	Josephine Busatti	Plaster
US2896715 *	May 5, 1952	Jul 28, 1959	Phillips Petroleum Co	Hydraulic cements
US3414420 *	Jan 28, 1965	Dec 3, 1968	United States Steel Corp	Oil well cement and method of making the same

US3432317 *	Jan 25, 1967	Mar 11, 1969	Martin Marietta Corp	Hydraulic cement mix containing saccharide polymers
US3486960 *	Sep 24, 1965	Dec 30, 1969	Tile Council Of America	Mortar compositions and methods of use
US3905826 *	Jan 8, 1974	Sep 16, 1975	Mexicano Inst Petrol	Setting retarder composition for use in cementation and recementation of cased oil wells
US4302251 *	Nov 26, 1979	Nov 24, 1981	Denki Kagaku Kogyo Kabushiki Kaisha	Cement composition containing dextrin

* Cited by examiner

CLASSIFICATIONS

U.S. Classification	106/730, 106/217.3, 106/126.1, 106/205.9
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