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2,745,759

CEMENTITIOUS COMPOSITION

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The present invention relates to so-called magnesia cements by which term it is intended to include both magnesium oxychloride and magnesium oxy-sulphate cementitious materials. More particularly, it relates to the use of additive ingredients in such materials for controlling or retarding the setting of the material and for stabilizing the products made therefrom.

Magnesium oxychloride cements have long been known. They are obtained by adding a solution of magnesium chloride to magnesia, i. e. magnesium oxide, a suitable inert filler, consisting of coarse aggregate, sand, wood flour, cork, or the like, being admixed if desired. The name "Sorel" is sometimes applied to a cement thus made, or at least to certain forms thereof, after the name of the original discoverer. So-called magnesium oxy-sulphate cements are likewise well known, being obtained by mixing magnesia and magnesium sulphate, either in the commercial form known as Epsom salts or that of a naturally occurring mineral, such as Kieserite.

While thus long known, the use of such magnesium oxychloride and oxy-sulphate cements has been limited by several factors, one of these being their tendency to set rather rapidly, thereby shortening the time in which a workman can work or handle the cement. This characteristic is aggravated by warm weather, and while it can to some extent be controlled by specially processing the magnesia, it is desirable to avoid processing. Another limiting factor has been the unstabilized condition, or lack of strength, of such cements when set, as exhibited by their poor weathering characteristics, i. e. rapidly cracking, warping and breaking up. This is believed to be due to additional hydration and expansion after the cement has hardened or set.

Numerous attempts have been made over the years to overcome the foregoing difficulties which have been encountered in the use of magnesium oxychloride cements. Among recent proposals has been the addition to the mixture either of finely divided copper or of cuprous oxide (see Patents Nos. 2,054,984-7 to Dean S. Hubbell). It has also been proposed (see patent No. 2,351,641 to William E. Sohl et al.) to add, either with or without such admixture of powdered copper, a relatively insoluble phosphate of a divalent metal. As of interest in the present connection it is noted that in such last cited patent it is explicitly stated that the use of alkali or ammonium phosphates, such as sodium acid phosphate, "is definitely deleterious in magnesium oxychloride cements, e. g. in producing excessive expansion on hardening." I have discovered that despite the teaching of the prior art a highly stable form of magnesium oxychloride cement, as well as of magnesium oxysulphate cement, may be obtained, and at the same time the setting thereof retarded, by the inclusion of a limited relatively small amount of a soluble phosphate, preferably one of the polymers of sodium metaphosphate, NaPO_3 , such as sodium hexametaphosphate, also known as soluble sodium hexametaphosphate glass. The use of such additive ingredient, I have found, is particularly efficacious where the mag-

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nesium oxide is obtained by burning dolomite at a controlled temperature so as to leave the calcium carbonate found in the original raw material substantially unchanged in composition.

It will therefore be seen that one principal object of the present invention is to provide a method and means for controlling the setting time of a magnesium oxychloride or like cementitious material; while another equally important object is to stabilize the set product made from such material. A further object is the provision of a cementitious material having the characteristics just described as well as the resulting product made therefrom.

To the accomplishment of the foregoing and related ends, said invention, then, consists of the means herein-after fully described and particularly pointed out in the claims.

The following description sets forth in detail certain approved compositions of matter and methods of employing the same, such disclosed compositions and steps constituting, however, but several of various ways in which the principle of the invention may be used.

As already indicated, the principal ingredients of the present improved composition comprise magnesia, i. e. magnesium oxide (MgO), and magnesium chloride. The usual fillers employed in magnesia cements are of course acceptable in addition to such principal ingredients.

Of the latter the magnesia, as likewise previously indicated, will preferably be that obtained by partially calcining dolomite which has been heated to a temperature of about 1400°F . so that, except for a small amount of impurities, it is essentially magnesium oxide and calcium carbonate. If the dolomite be burned at too high a temperature, calcium oxide will also be produced, which is ordinarily objectionable. However, by the practice of the present invention, the presence of such calcium oxide can be tolerated within reasonable limits, so that the processing of the dolomite is no longer so critical a matter. Magnesia, by itself, can be substituted for such partially calcined dolomite, either entirely or in an amount equal to that found in such partially calcined dolomite. In the latter case, the difference in weight between the magnesium oxide and the dolomite may be made up by the addition of calcium carbonate as a filler. In the same way magnesian limestones in which the ratio of magnesium to calcium carbonate is lower than that in dolomite, may be utilized by burning to the indicated extent and then adding the proper amount of magnesia.

The foregoing ingredient, whether obtained by directly calcining dolomite to the degree indicated or otherwise made up, should be in a finely divided or pulverized form in order to mix readily with the magnesium chloride solution. The latter will preferably have a concentration of from about 22°Baume up to a completely saturated solution. A solution of appreciably less than the indicated minimum strength is undesirable as it will not result in a hard cementitious product.

Also, as previously indicated, I include in the present improved composition a water soluble phosphate compound such as the previously described sodium hexametaphosphate, for which may be substituted, as an equivalent, either sodium polyphosphate, sodium tripolyphosphate, monobasic sodium phosphate or dibasic sodium phosphate. The phosphate compound should be finely ground or powdered so that it will be readily dissolved in the wet mix or in the magnesium chloride solution when making up the cementitious composition.

In making up such cementitious mixture the amount of partially burned or calcined dolomite, i. e. mixture of magnesium oxide and calcium carbonate, in relation to the magnesium chloride solution is important. Excellent results have been obtained by using about one part by weight of the dolomite to from about 0.6 to 0.975 part by

weight of 22° Baumé magnesium chloride solution which are the preferred ratios. However, the amount of the magnesium chloride solution used can be varied appreciably, the main criterion here being of course the workability of the resulting mix. In any event the above stated proportions will vary in accordance with changes in the solution (Baumé) strength of the magnesium chloride solution.

Only a very small amount of the soluble phosphate additive is required to produce satisfactory magnesium oxychloride cements, made up of the foregoing principal ingredients. Thus as little as 0.05% by weight of the dry water soluble phosphate based on the dry weight of the partially calcined dolomite has been found sufficient. However, I prefer to use not less than about 0.2% of soluble phosphate in order to insure obtaining a cement having an acceptable setting time or strength. Excellent products have been obtained using concentrations of from 0.2% to about 1.5% by weight of soluble phosphates, and this represents the preferred range.

It will be understood that one or more of the soluble phosphates indicated as suitable for use may be used individually or together. Such soluble phosphate or phosphates may be added in dry state to the partially calcined dolomite and such mixture will constitute a partially prepared form of my improved composition, the latter being completed upon the addition thereto of the magnesium chloride solution as above specified. It is also possible to add the soluble phosphate or phosphates to such magnesium chloride solution and add the resulting solution to the partially calcined dolomite. Indeed, the soluble phosphate may be added to the magnesium oxychloride mixture resulting from the addition of the magnesium chloride solution to the partially calcined dolomite, but this is not the preferred procedure for the obvious reason that such mixture immediately begins to set.

The following are examples of various cementitious compositions, embodying the present improvement, which have been actually prepared and tested as indicated.

A magnesium chloride solution of 22° Baumé was added to partially calcined dolomite in the ratio of 0.6 part by weight of solution to 1.0 part by weight of partially burned dolomite and the mixture agitated. The slurry was then separated into several parts. To each, except one, a determined amount of a soluble phosphate was added, the mix agitated, and the cement was cast into the shape of a brick. The set retarding properties of these cements and their tensile strengths 24 hours after casting were observed. The work was conducted at a temperature of 78° F. and at a relative humidity of 50%. The results are shown in the following table:

Table 1

Percent by Weight of Addition Agent	Tensile Strength, lbs./sq. in.	Set Retarding Properties, Time in Hours	
		Initial	Final
None	125	1.9	2.2
0.2 Sodium hexametaphosphate	458	2.2	3.5
0.5 Sodium hexametaphosphate	460	2.4	3.65
1.0 Sodium hexametaphosphate	328	4.3	6.55
0.2 Sodium Tripolyphosphate	369	2.0	2.95
0.5 Sodium Tripolyphosphate	417	2.2	2.7
1.0 Sodium Tripolyphosphate	304	2.65	3.9
0.2 Sodium polyphosphate	428	1.75	2.75
0.5 Sodium polyphosphate	371	2.0	3.0
1.0 Sodium polyphosphate	365	3.9	4.45

The foregoing results show not only that magnesium oxychloride cements containing fractional amount of soluble phosphate compounds are many times stronger than similar cements without such phosphates, but also that adequate setting time can be made available to permit the casting, troweling, and working of the cement before final setting and hardening.

Cements similar to those of the preceding example were prepared using the same ratio of magnesium chloride solution to partially calcined dolomite with the maintenance of the same operating conditions. These cements contained, however, only 0.5% by weight of soluble phosphates. One lot of the cast cements was stored in air while the other lot was stored in water. The condition of these cements was examined after twenty-one days, and their tensile strengths were determined after 28 days. The results are shown in the following table:

Table 2

Percent by Weight of Addition Agent	Condition After Storage for 21 Days		Tensile Strength, lbs./sq. in. After 28 Days	
	In Air	In Water	Aged in Air	Aged in Water
None	Cracked	Cracked	Cracked	Cracked
0.5 Sodium hexametaphosphate	No signs of disintegration.	No signs of disintegration.	490.	70.
0.5 Sodium tripolyphosphate	do	do	610	105.
0.5 Sodium polyphosphate	do	do	490	50.

With only fractional amounts of a soluble phosphate compound in a magnesium oxychloride cement, it is self-evident from the foregoing example that the tensile strengths thereof are extremely high after aging in air and satisfactory after aging in water when compared with specimens having no soluble phosphate therein.

Magnesium oxychloride cements were prepared according to the procedure of the first example, except that monobasic sodium phosphate, powdered copper, and tertiary calcium phosphate were the respective addition agents used. One cement was also cast without any addition agent therein. The setting times of these cements were observed and their tensile strengths obtained after storage in air for nine days. The following results were obtained:

Table 3

Percent by Weight of Addition Agent	Setting Time In Hours		Tensile Strength, lbs./sq. in.
	Initial	Final	
None	1.75	4.75	Cracked.
0.05 Monobasic sodium phosphate	2.5	3.75	245.
0.1 Monobasic sodium phosphate	3	4.0	270.
0.2 Monobasic sodium phosphate	3.5	4.5	280.
0.3 Monobasic sodium phosphate	4.5	5.5	355.
0.5 Monobasic sodium phosphate	5.5	6.5	455.
10.0 Powdered Copper	1.75	5	120.
1.0 Tertiary calcium phosphate	6	15	10.

¹ Cracked after 5 days.

From the foregoing example it is evident that magnesium oxychloride cements without soluble phosphates, or containing copper or insoluble phosphate compounds, may crack altogether or have considerably less tensile strength after curing in air than cements containing water soluble phosphates. The copper containing body had a tensile strength less than one-half of that of the soluble phosphate containing bodies even with 20 to 200 times more copper than soluble phosphate.

It should be noted, with respect to the cements containing soluble monobasic sodium phosphates, that an increase in the amount of the phosphate from 0.05 to 0.5% in the magnesium oxychloride cements not only produces an increase in their total setting times but also a corresponding increase in their tensile strengths.

Cements were prepared according to the method disclosed in the first example, except that sodium hexametaphosphate was the only addition agent used. After storing in air for fourteen days, the volume changes and warping of the cements were determined. Warping was calculated

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at 100 times the maximum height of curvature of a ten inch bar; the volume of each sample was determined at the beginning and at the end of the test period and the change expressed as a percentage of the former. The results are shown below:

Table 4

Percent by Weight of Addition Agent	Volume Change	Warping
None.....	7.8	Cracked.
0.25.....	2.0	24.
1.0.....	1.1	18.

The foregoing results again show that the volume change and warpage factors of the cements containing soluble phosphates are substantially better than a cement having no soluble phosphate addition.

The effect of the presence of calcium oxide, which is well known to be deleterious in magnesium oxychloride cements was investigated. Cements were prepared according to the process described in the first example, except that one lot contained only calcium oxide as the addition agent while the other lot contained calcium oxide and also sodium hexametaphosphate. Moreover, one cement was cast without any addition agent. The samples were observed for twenty-seven days and the tensile strengths thereof, based on an average of three samples, are indicated below:

Table 5

Percent by Weight of Addition Agent	Percent by Weight Calcium Oxide	Tensile Strength in lbs./sq. in.
None.....	0	10
Do.....	1.0	119
Do.....	3.0	111
Do.....	5.0	13
1.0 Sodium hexametaphosphate.....	0.0	452
Do.....	1.0	490
Do.....	3.0	337
Do.....	5.0	350

¹ Extensive cracking after four days.

From the foregoing it is apparent that the stability of magnesium oxychloride cements containing calcium oxide additions, varying in amount from one to 5.0 per cent, was improved markedly by the addition of 1.0% of sodium hexametaphosphate. The control series, containing no phosphate, but the same calcium oxide additions, cracked after four days; this is not unexpected from the fact that it is well known that magnesium oxychloride cements ordinarily fail when small amounts of calcium oxide are present, due, for example, to overburning of dolomite, or magnesite containing calcium carbonate. These observations are of considerable interest from the commercial standpoint, indicating, as they do, that the presence of calcium oxide as a result of such overburning, should exert no appreciably deleterious influence on the set-retarding or stabilizing properties of magnesium oxychloride cements containing soluble phosphates.

The effect of storage on the properties of a dry mix were investigated by adding one per cent by weight of soluble dry phosphate to dry partially calcined dolomite, and after thirty days adding 22° Baumé magnesium chloride solution to the dry mixture in the ratio one part dolomite to 0.975 part magnesium chloride solution. A filler, coarse aggregate, was also added in ratio of three parts of filler to one part dolomite. As a comparison, cements were also prepared in the same manner and cast immediately without any aging of the dry mix. After casting, the specimens were aged in air for twenty-eight days at a temperature of 80° F. and at a relative humidity of 50%. The results show that the storage of dry compositions does not affect the tensile strengths of the cements containing soluble phosphates.

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Other tests involving the use of corresponding amounts of insoluble phosphates, in place of the herein specified soluble phosphates, show the latter to be markedly superior both in control of setting time and tensile strength of the resulting product. It has also been determined by actual test that the adding of a soluble phosphate in the amount of 2% and over does not increase, but actually reduces, the tensile strength of the resulting cement.

Results directly comparable to those shown in the foregoing examples are obtained where magnesia is used instead of the partially calcined dolomite. Thus the following table shows the effect of adding a small amount of soluble phosphate to test specimens made of mixing magnesia and 22° Baumé magnesium chloride solution in 1 to 1 ratio:

Table 6

Percent by Weight of Addition Agent	Tensile Strength in lbs./sq. in.	Volume Change	Warping
None.....	100	-4.1	48.0
0.25 Sodium hexametaphosphate.....	230	-1.2	1.4
1.0 Sodium hexametaphosphate.....	290	-0.6	3.0

Referring to the preceding table, the determination of tensile strength, volume change and warping was, as in the case of a preceding example, made after a fourteen day interval and the warping was calculated at 100 times the maximum height of curvature of a ten inch bar.

Tests on the order of those described above in connection with magnesium oxychloride cements have also been made with magnesium oxysulphate cements by similarly adding thereto indicated small amounts of a water soluble inorganic phosphate. As a specific example, a cement having the following composition, viz. 43.4% partially calcined dolomite, 13.2% magnesium sulphate ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$), and 43.4% stone aggregate as a filler, was made and tested for strength with and without the addition of 0.2% sodium hexametaphosphate with the results shown in the following table:

Table 7

Percent by Weight of Addition Agent	Tensile Strength in lbs./sq. in.	
	After 7 Days	After 14 Days
None.....	217	413
0.2 Sodium hexametaphosphate.....	380	550

As will be clear from the foregoing table, a very substantial increase in tensile strength is obtained by the use of the additive.

While it is not precisely understood what chemical or physical role is played by these soluble phosphates when mixed in the indicated small amount with the magnesium oxychloride or magnesium oxysulphate cementitious materials as described, it is thought possible that they act to produce a more stable crystal structure by retarding the immediate formation of a hard product until a complete crystal lattice is developed or until all the water of crystallization has been taken up by the magnesium oxychloride or oxysulphate, as the case may be. It may also be possible that there is a chemical reaction involved here, or a chemical combination between the phosphates and the magnesium oxychloride or oxysulphate cementitious material.

In the light of the previously given description, it will be understood that the term "magnesia cement" includes both magnesium oxychloride and magnesium oxysulphate cementitious material. It will also be understood that the term "partially burned dolomite" as used herein connotes a corresponding mixture of magnesium oxide and calcium

carbonate whether it be obtained directly by calcining dolomite or otherwise. Similarly, the term "water soluble phosphates" will be understood to connote any of the several phosphates heretofore described in connection with the examples given or otherwise. Finally, the term "stabilized" as applied to the resulting cementitious product will be understood to connote a product having generally the stable qualities after setting exhibited by the cements obtained by use of the present improved composition in the examples given above.

Other modes of applying the principle of my invention may be employed instead of the one explained, change being made as regards the process herein disclosed or the materials employed in carrying out the process, provided the step or steps stated by any of the following claims or the equivalent of such stated step or steps be employed.

I therefore particularly point out and distinctly claim as my invention:

1. A slow-setting cementitious composition consisting essentially of an admixture of magnesium oxide and calcium carbonate in the approximate weight ratio that the same are found in partially calcined dolomite substantially free of calcium oxide, an aqueous solution of a reagent selected from the group consisting of magnesium chloride and magnesium sulphate in an amount sufficient to form a workable mass with said admixture, the concentration of said reagent being from about 22° Baumé to complete saturation, and from about 0.05% to about 1.5% by weight, based on the weight of said admixture, of a water-soluble, alkali metal phosphate.

2. A slow-setting cementitious composition consisting essentially of an admixture of magnesium oxide and calcium carbonate in the approximate weight ratio that the same are found in partially calcined dolomite substantially free of calcium oxide, magnesium chloride solution in an amount sufficient to form a workable mass with said admixture, the concentration of such reagent being from about 22° Baumé to complete saturation, and a water-soluble, alkali metal phosphate in an amount of

from about 0.05% to about 1.5% by weight based on the weight of said admixture.

3. A slow-setting cementitious composition consisting essentially of one part by weight of an admixture of magnesium oxide and calcium carbonate in the approximate weight ratio that the same are found in partially calcined dolomite substantially free of calcium oxide, from 0.6 to 0.975 part by weight of approximately 22° Baumé to saturated magnesium chloride solution, and from 0.05% to 1.5% by weight, based on the weight of said admixture, of a compound selected from the group consisting of sodium monobasic phosphate, sodium dibasic phosphate, sodium hexametaphosphate, sodium polyphosphate, and sodium tripolyphosphate.

4. A stabilized magnesium oxychloride cementitious material, consisting essentially of magnesium oxychloride, prepared from one part by weight of partially calcined dolomite substantially free of calcium oxide and from 0.6 to 0.975 part by weight of approximately 22° Baumé to saturated magnesium chloride solution, and from 0.3% to 0.5% by weight, based on the weight of said dolomite, of a compound selected from the group consisting of sodium monobasic phosphate, sodium dibasic phosphate, sodium hexametaphosphate, sodium polyphosphate, and sodium tripolyphosphate.

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