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PROCESS FOR PRODUCING AERATED CEMENTITIOUS COMPOSITIONS AND ARTICLES

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This invention relates to hydraulic cements with a quick set and hardening such as Portland cement, cements of the high alumina series, the oxychlorides of zinc and magnesia and to such other cements as plaster of Paris, and the like, in which aeration, e. g. the formation of pores, voids, cells or gaps is accomplished by means of evolving oxygen gas from solid substances containing this gas in oppositely polar conditions.

In addition to the ordinary state in which oxygen is known with its usual neutral properties it also exists in another state, that of allotropic oxygen or as it is generally called, ozone. It is also known that certain peroxides such as those belonging to the class of the peroxide of manganese, or the latter's permanganates of the alkali metals such as the potassium permanganate and the like, the peroxide of lead and also the chromic anhydride commonly called chromic acid, or the latter's salts such as potassium dichromate and the like, on the one hand and those belonging to the class of peroxides of barium and sodium on the other, contain oxygen which produces ozonic effects but of which the oxygen of each individual class possesses different properties. The peroxides of lead and of manganese produce chlorine with hydrochloric acid and liberate oxygen when heated. Chromic acid when added to the acidified water in the electrolytic decomposition of water increases the production of ozone and it transforms camphene into camphor with evolution of oxygen. Peroxide of manganese gives a blue colour to the precipitated resin of guaiacum and turns aniline (on paper) brown. It does not produce peroxide of hydrogen but when mixed with the latter even at a strength of only three per cent by volume it decomposes it with slow liberation of oxygen gas. With sulphuric acid it produces a rich series of purple colours with strychnia. Barium peroxide similarly treated does not produce the results above described but it does produce hydrogen peroxide with hydrochloric acid without liberating chlorine; its oxygen in its action on alkaline iodides and in its bleaching properties resembles ozone. Sodium peroxide by the action of water evolves oxygen and also produces hydrogen peroxide. Generally the oxygens of each one individual class exercise no action upon each other when treated with an acid but when a peroxide of the first class is brought into contact with one of the second class oxygen gas may be evolved abundantly and with great rapidity even with almost explosive violence either by the use of an acid such as for example hydrochloric or even without the use of an acid. For instance when a mixture of manganese peroxide of the first class with barium peroxide of the second class is treated with hydrochloric acid their two oxygens neutralize each other and evolve oxygen gas, and when chromic acid, also the first class, is present, this evolution is of greatly increased intensity, a phenomenon similar to that as with the electrolysis of water when the acidified water contains a little chromic acid and more ozone is obtained than without it. Manganese peroxide with hydrogen peroxide, which latter also belongs to the second class, evolves oxygen but not rapidly. Although thus dealing with peroxides in both cases the oxygen as it is evolved must be different in its properties. In the electrolytic decomposition of water the oxygen which appears at the positive platinum pole has ozonic properties and has been found to possess the same power of colouring strychnia as the oxygen (ozone) liberated by sulphuric acid from the peroxide of manganese or from the latter's permanganates of the alkali metals, from peroxide of lead and from chromic acid, or the latter's salts such as potassium dichromate and the like. The oxygen of this class of peroxides and of chromic acid and its salts has thus been considered to be an electro-negative element, per contra the oxygen of the peroxides of the second class as electro-positive elements.

The evolution of oxygen gas can be accomplished by mixing a compound such as hydrogen peroxide and alkali peroxide with manganese peroxide in this process. However, the manganese peroxide itself does not undergo any change, but merely exercises a catalytic action resulting in the liberation of oxygen from the other peroxides present. In this process, manganese peroxide remains after completion of the aeration as a black residue which may entirely spoil the color of the resulting composition.

If the manganese peroxide in the above described process is replaced by potassium permanganate which is able to liberate the active oxygen of the hydrogen peroxide, for example, the potassium permanganate undergoes a chemical change in the process. However, the chemical reaction involved leaves an insoluble, voluminous, greenish-brown residue of potassium manganate and manganous oxide which also seriously affects the color of the resulting product.

According to my invention I mix barium peroxide and manganese peroxide intimately together and I incorporate this mixture with a

cement such as for example plaster of Paris. To this mix of plaster of Paris and peroxides of barium and manganese I add water in the usual manner and proportion and stir the mix to a thick and creamy consistency and then add thereto a reagent solution containing chromic acid and hydrochloric acid to promote the evolution of oxygen gas from the peroxides contained therein. I thereafter stir the whole mass rapidly and thoroughly either by hand or mechanically when a powerful aeration of a few seconds duration sets up in the mass which I then rapidly pour into moulds which may be of metal, wood, paper and the like. By varying the percentage of the reagent solution the aeration may at will be either intensified, retarded and/or accelerated and if so required may be stabilized by the addition of a small quantity of casein, rosin soap, saponin, albumen and the like. If circumstances require the acid solution may be ultimately neutralized by the use in the cement and/or plaster of Paris of caustics, alkaline earths or salts and the like. The article thus produced is then submitted to the usual treatment of drying and hardening.

Manganese peroxide when used in conjunction with barium peroxide in the presence of hydrochloric acid does not act as a catalyst, but is decomposed into a soluble manganese salt leaving no residue to cause discoloration of the article produced. Potassium permanganate when used in conjunction with barium peroxide in the presence of hydrochloric acid is also decomposed into soluble salts presenting a clear solution with no residue whatsoever.

The method followed by the present invention aims at evolving oxygen gas and using it forthwith in its "nascent" state, e. g. directly and immediately on its evolution and in its full power of action therefore without wasting any of its energy resulting in an economical commercial application.

I do not bind myself to the use of manganese peroxide alone for I may also use in its stead its permanganates of the alkali metals such as the potassium permanganate and the like. Nitric acid may be used instead of hydrochloric acid.

As an example the following compounding weights and volumes per 6800 lbs. of aerated plaster of Paris will illustrate the process.

(*a*) 45 lbs. of barium peroxide and 3¼ lbs. of manganese peroxide are thoroughly mixed together for a short while by preference in a small ball mill. Thereafter 4 lbs. and 13 ounces of this mix are thoroughly mixed in the usual manner with 6800 lbs. of dry plaster of Paris. The plaster of Paris thus prepared is then drawn on a belt in the usual manner through a water bath in order to soak it with water to a workable consistency and to convey it in the state of a semi-fluid mass to the mixer. Immediately before the said semi-fluid mass reaches the mixer I add thereto about 24 gallons of a solution consisting of:

Commercial hydrochloric acid	gallons	3
Water	do	22
Chromic acid	ounces	27

The semi-fluid mass thus prepared now passes through a powerful beater-mixer for a few seconds duration when an equally distributed powerful aeration of the plaster mass results through the evolution and dispersion of oxygen gas in its "nascent" state.

I do not limit myself to the weights and volumes as given in the example for it should be understood that by varying their ratios the aeration may at will be either intensified, retarded and/or accelerated.

I have, however, found that to obtain a thorough homogeneous mix of such a small quantity as 4 lbs. and 13 ounces of barium and manganese peroxide mix with 6800 lbs. of dry plaster of Paris is a rather troublesome operation. I therefore give preference to the execution of the aeration principle in the following manner which consists in using solutions only instead of partly a dry powder mix and partly a solution. To this effect I split the 3 gallons of commercial hydrochloric acid solution in 22 gallons of water as stated in the aforementioned example sub (*b*) into two parts each of 1½ gallons of commercial hydrochloric acid and 11 gallons of water. In one half part, e. g. 12½ gallons hydrochloric acid solution I dissolve 4½ lbs. of barium peroxide. In the second half part of 12½ gallons of hydrochloric acid solution I dissolve 27 ounces of chromic acid and 5 ounces of manganese sulphate instead of 5 ounces of manganese peroxide which latter with hydrochloric acid would produce chlorine which is to be avoided. In other words I substitute the latter by the former.

The two solutions are prepared separately in two vats or containers suitable for the purpose and the adding of each of them at the rate of about 1 gallon per 5 minutes to the semi-fluid plaster mass immediately before it reaches the mixer proceeds in the same manner as hereinbefore stated with the difference however that the barium peroxide solution is added to it a little distance apart from the chromic acid solution so that the two do not enter into contact but upon entering the beater-mixer where the energetic action of the latter instantly promotes in the same manner a powerful aeration due to the evolution and dispersion of oxygen gas in a "nascent" state. Here again I do not bind myself exclusively to the aforementioned weights and volumes which may be varied to suit the degree of aeration one wishes to attain.

In that part of the 12½ gallons commercial hydrochloric acid solution which contains 27 ounces of chromic acid and 5 ounces of manganese sulphate, I can advantageously substitute for both the 27 ounces of chromic acid together with the 5 ounces of manganese sulphate, solely 22 ounces of a chromic acid salt such as for instance potassium dichromate or 16½ ounces of an alkali metal permanganate of the manganese peroxide such as potassium permanganate, but since potassium permanganate is the more economical I therefore give preference to the use of potassium permanganate. Moreover, when using potassium permanganate, the aeration bubbles which form at the moment of the evolution of the gas are much more infinitesimal in size but far greater in number, e. g. they lend themselves to a far greater dispersion throughout the cement mass or slurry in which they are imprisoned thereby forming a cellular product of higher technical value and efficiency. This is of great importance for instance when plaster of Paris cement slurry is poured into paper moulds such as is the case with plaster boards. If the aeration pores or cells are relatively large and fewer in number, the boards will lose in strength but when they are structured so as to represent a multitude of homogeneously interspersed but contiguous microscopic voids or

cells, the boards will be stronger and have higher thermal and acoustical value.

The liquid reagents per 6800 lbs. plaster per hour herebefore described may thus also be composed on the one hand of 11 gallons of water, 1½ gallons of commercial hydrochloric acid and 4½ lbs. of barium peroxide dissolved therein, and on the other of 11 gallons of water, 1½ gallons of commercial hydrochloric acid and 16½ ounces of potassium permanganate or 22 ounces of potassium dichromate dissolved therein. The two solutions are then ready to be used.

I do not bind myself exclusively to the aforementioned weights and volumes which may be varied to suit the degree of aeration one wishes to obtain.

When using Portland cement or cements of the high alumina series or of the oxychlorides of zinc or of the magnesia series the proportion of cementitious material is the same as hereinbefore described.

I claim:

1. Process for producing aerated cementitious compositions and articles made therefrom, comprising the steps of mixing together cementitious material, barium peroxide, an acid substance selected from the group consisting of hydrochloric acid, nitric acid and the mixtures of hydrochloric with nitric acid, a compound selected from the group consisting of manganese peroxide, the alkali metal permanganates, chromic acid and the chromic acid salts, and sufficient water to form a semi-fluid mixture, and stirring the mixture to promote dispersion throughout the semi-fluid mixture of the evolved oxygen, the proportions of the several reagents being such as to result in the evolution of oxygen in a nascent form.

2. Process for producing aerated cementitious compositions and articles made therefrom, comprising the steps of intimately mixing cementitious material, barium peroxide, and manganese peroxide with a quantity of water sufficient to bring the mixture into a semi-fluid state, then adding an acid substance selected from the group consisting of hydrochloric acid, nitric acid, and the mixtures of hydrochloric with nitric acid and stirring to promote dispersion throughout the semi-fluid mixture of the evolved oxygen, the proportions of the several reagents being such as to result in the evolution of oxygen in a nascent form.

3. Process for producing aerated cementitious compositions and articles made therefrom, as claimed in claim 1, in which an alkali metal permanganate is admixed to said acid substance, before the latter is added to said semi-fluid mixture.

4. Process for producing aerated cementitious compositions and articles made therefrom, as claimed in claim 1, in which a chromic acid is admixed to said acid substance, before the latter is added to said semi-fluid mixture.

5. Process for producing aerated cementitious compositions and articles made therefrom, as claimed in claim 1, in which a chromic acid salt is admixed to said acid substance, before the latter is added to said semi-fluid mixture.

6. Process for producing aerated cementitious compositions and articles made therefrom, comprising the steps of dissolving barium peroxide in a diluted acid substance selected from the group consisting of hydrochloric acid, nitric acid and mixtures of hydrochloric with nitric acid, dissolving an alkali metal permanganate in a diluted acid substance selected from the group consisting of hydrochloric acid, nitric acid and the mixtures of hydrochloric with nitric acid, adding the two solutions separately to a semi-fluid mass consisting of cementitious material and water, and stirring the mixture to promote dispersion throughout the semi-fluid mass of the evolved oxygen, the proportions of the several reagents being such as to result in the evolution of oxygen in the nascent form.

7. Process for producing aerated cementitious compositions and articles made therefrom, comprising the steps of dissolving barium peroxide in a diluted acid substance selected from the group consisting of hydrochloric acid, nitric acid and mixtures of hydrochloric with nitric acid, dissolving a chromic acid in a diluted acid substance selected from the group consisting of hydrochloric acid, nitric acid and the mixtures of hydrochloric with nitric acid, adding the two solutions separately to a semi-fluid mass consisting of cementitious material and water, and stirring the mixture to promote dispersion throughout the semi-fluid mass of the evolved oxygen, the proportions of the several reagents being such as to result in the evolution of oxygen in the nascent form.

8. Process for producing aerated cementitious compositions and articles made therefrom, comprising the steps of dissolving barium peroxide in a diluted acid substance selected from the group consisting of hydrochloric acid, nitric acid and mixtures of hydrochloric with nitric acid, dissolving a chromic acid salt in a diluted acid substance selected from the group consisting of hydrochloric acid, nitric acid and the mixtures of hydrochloric with nitric acid, adding the two solutions separately to a semi-fluid mass consisting of cementitious material and water, and stirring the mixture to promote dispersion throughout the semi-fluid mass of the evolved oxygen, the proportions of the several reagents being such as to result in the evolution of oxygen in the nascent form.

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