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RETARDER FOR CEMENTITIOUS MATERIAL

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The present invention relates to an improved retarder for use with cementitious material, particularly calcined gypsum plasters.

More particularly, the invention concerns itself with a stabilized plaster comprising a major portion of calcium sulfate hemihydrate and a minor portion of set-modifying improved "age-stabilized" reagents made in accordance with the present invention. Such a plaster containing the improved set-modifying and age-stabilized reagents is characterized by its ability to withstand the effect of aging upon storage for a long period of time without any marked change in the setting characteristics of the material.

This invention is to be distinguished from those inventions which relate to so-called set-stabilized plasters, by which is meant plasters the set of which is not adversely affected by adventitiously therewith admixed accelerating and retarding influences, but the present invention relates rather to a plaster the setting time of which is predetermined and which will set in substantially the same time when mixed under the same conditions two months after manufacture or twelve months after manufacture. In other words, if the plaster has been adjusted by the addition of the retarding reagent of the present invention so as to set, for example, in three hours, the setting time at the end of twelve months' storage will not have increased very substantially or at the most will set in four or five hours, while it is well known that ordinary retarded plaster upon aging becomes slower and slower setting, and therefore the user must have a fair idea of the age of the plaster in order to know what to do to give it the desired setting time. This change in the setting time of the plaster seems to be due to a number of factors but probably to a change in the retarder itself rather than to changes in the inorganic constituents of the plaster.

As an example of the difficulties hitherto encountered with ordinary retarded gypsum plasters, it might be stated that, for instance, freshly prepared plaster the time of set of which has been adjusted to two hours will in the course of only four weeks' storage under ordinary atmospheric conditions, but protected from rain, lengthen in time of set to about eight hours.

The following table indicates the effects of the improved age-stabilized reagents upon a commercial plaster aged under atmospheric conditions. The time of set in this table is that of mixtures containing $2\frac{1}{2}$ parts of water-washed sand.

TABLE 1

Time of set—hours

Age.....	Fresh	2 months	6 months
Normal plaster.....	5	12	13
Improved plaster.....	5	7	8

It has been found that the improved reagent of the present invention exerts equally effective stabilization against deterioration upon aging even in the so-called "stabilized" plasters, as for example such a one as is described in United States patents to George D. King, Nos. 1,989,641 and 2,078,198. The following table shows the effect of the improved age-stabilized reagents on such a stabilized plaster:

TABLE 2

Time of set—hours

Age.....	Fresh	2 months	6 months
Plaster of Patent No. 1,989,641.....	5	10	11
Same+improved "age-stabilized" reagent.....	5	6	$6\frac{1}{2}$
Plaster of Patent No. 2,078,198.....	8	13	14
Same+improved "age-stabilized" reagent.....	8	$8\frac{1}{2}$	$9\frac{1}{2}$

In Table 2 the retarder of the present invention was substituted for an equal amount of the retarder mentioned in the patents. While the invention will be illustrated in its application to a calcined gypsum material such as the ordinary calcium sulfate hemihydrate plaster, it is not intended to confine or limit it thereto, for it can obviously be applied with corresponding effect to all compositions containing either soluble anhydrite or calcium sulfate hemihydrate, such as dental plasters, orthopedic plasters, etc.

One of the objects of the present invention therefore is to modify the ordinary nitrogeous set-retarding materials so as to render them substantially nonhygroscopic or at least of diminished tendency to absorb moisture from the air, or perhaps, stated another way, to render them sufficiently water repellent so that they will not lump or gather together in the plaster because of the fact that they are mixed with or coated with, or both, a water-repellent material of the nature of a soap, either soluble or insoluble. In case a film of soap is associated with the retarder particles, this will repel moisture, but not to such an extent as to preclude the solubility of the material when the plaster is mixed with water, for

when this is done, sufficient water dialyzes through the soapy membrane to distend or swell the retarded particles, thereby disrupting the moisture-repellent film and allowing the retarder to go into solution. The incorporation of the soap or other water-repellent material with the retarder is carried out as a part of the process or a step in the process of manufacturing the retarder itself.

In order that the present invention may be more readily understood, it is believed advisable to describe the manner of carrying it out by reciting briefly the methods hitherto employed for the preparation of an organic nitrogenous retarder. Thus, for example, ground keratinaceous material such as hair, hoofs, or the like, is treated with a concentrated solution of sodium hydroxide for a period of hours until decomposition of the material has been effected. The thus decomposed material then has added to it finely ground quicklime (calcium oxide) in a sufficient quantity to dehydrate the solution by the formation of calcium hydroxide, and, by the evaporation of water as a result of the heat liberated by the reaction of the lime with the water in the mixture, the calcium hydroxide formed acts as an extender or carrier for the very active protein material obtained by the hydrolysis of the keratinaceous raw material. If a proper quantity of lime has been used, the final product is a dry granular material of such consistency that no further artificial drying is required, but the product may be ground to desired degree of fineness suitable for incorporation with the plaster.

In carrying out the present invention, however, the hydrolyzed keratinaceous material is modified at that step of the process which just precedes the addition of the quicklime. Thus the hair, hoofs, and the like, are digested in the time-honored manner with a suitable alkali, and when the hydrolysis has been effected, and before the quicklime is added, there is introduced into the mixture a soap or a substance capable of producing soap, the hydrolyzed keratinaceous material then being thoroughly mixed with the added substances. The addition of the soap or soap-forming ingredients may be carried out either cold or hot but preferably while the material is still warm, following the hydrolyzing reaction. After the soap has been added or formed, the quicklime is added in the usual way to produce the final dry retarder material.

By the term "soap" as used herein it is intended to include the salts of long-chain aliphatic acids such as stearic acid, palmitic acid, oleic acid, and the like. Although water-soluble types of soap are preferable, it has been found that water-insoluble soaps such as calcium stearate, aluminum stearate, or the corresponding oleates or other fatty acid salts of somewhat similar molecular weight may also be employed. In place of soap, it has been found that other water-repellent materials such as waxes, waxy materials, fats, and oils may be used. For practical purposes it is preferred to use about 10% of soap or water-repellent material, based upon the weight of the keratin used, but obviously the amount may be considerably varied without departing from the scope of the present invention. It is not definitely known in what manner the addition of the soap or water-repellent material aids in stabilizing the retarder, and no theory is advanced other than that briefly mentioned hereinabove. It is not intended that the inven-

tion be in any way circumscribed by any particular theory.

As an alternative method—that is, instead of adding the soap or water-repellent material to the hydrolyzed keratin prior to the addition of the lime or other extending agent—it is possible to add the soap or water-repellent material simultaneously with the addition of the quicklime. However, the addition of soap after liming or during liming is not as effective as adding it first, because in the former case a really efficient dispersion or solution of the soap is not obtained.

Although the illustrations hereinabove are given in connection with age-stabilized retarders produced from keratinaceous retarders, it has been found that the effect of the soap is similar when used in connection with retarders prepared from other proteins of either vegetable or animal origin, such, for example, as may be made from vegetable protein derived from soy beans, peanuts, beans, castor beans, corn, etc. In such case, the hydrolyzed protein may have the soap incorporated therewith by formation of the soap during the alkaline hydrolysis of the protein-containing material as the result of saponification of the oil, or residual oil, contained in the raw material employed. When using, for example, a soy bean meal containing some residual oil, the action of the alkali employed in the hydrolysis of the protein portions of the soy bean flour will combine with the oil contained in the flour with the formation of a soap. The general preparation of retarders from such vegetable proteins is, however, disclosed and claimed in the copending application of Elmer B. Oberg, Serial No. 168,913, filed on October 14, 1937.

The present invention is to be sharply differentiated from any process in which soap as such is added to the cementitious plaster composition as a separate thing from the addition of the retarder. It is known that soap has been used to waterproof plasters and cements as such, and the invention does not concern itself with any such process but only with the addition of soap or water-repellent materials to the retarder itself as a step in its preparation.

What is claimed is:

1. A retarder for plasters and the like comprising a hydrolyzed protein material and a water-repellent substance associated therewith in an amount substantially in excess of that amount derivable from the crude protein material hydrolyzed.

2. A retarder for plasters and the like comprising hydrolyzed keratin associated with a water-insoluble soap in an amount substantially in excess of that amount derivable from the crude keratin hydrolyzed.

3. A retarder for plasters and the like comprising a hydrolyzed protein material, an extender or carrier therefor and a water-repellent substance associated with the mixture to preserve the predetermined retarding effect of the material, said water-repellent substance being present in an amount substantially in excess of that amount derivable from the crude protein material hydrolyzed.

4. A stabilized set-retarding composition comprising a hydrolyzed protein, an inert extender or carrier therefor, and a water-insoluble water-repellent soap, said soap being present in an amount substantially in excess of that amount derivable from the crude protein hydrolyzed.

5. The process of producing an improved retarding composition for plasters and the like

which comprises hydrolyzing a proteid material, adding a water-repellent substance thereto, and drying the thus produced mixture.

5 6. The process of producing an improved re-
tarding composition for plasters and the like
which comprises hydrolyzing a proteid material,
adding a water-soluble soap thereto, then admix-
ing therewith a substance capable of converting
said soap into an insoluble water-repellent prod-
10 uct, and drying the mixture thus produced.

7. The process of producing an improved re-
tarding composition for plasters and the like
which comprises hydrolyzing a proteid material
containing a saponifiable oil so as to produce a
15 water-soluble soap therein, then admixing there-
with a substance capable of converting said soap
into an insoluble water-repellent product, and
drying the mixture thus produced.

8. The process of producing an improved re-
20 tarding composition for plasters and the like
which comprises hydrolyzing keratinaceous ma-
terial with an alkali, adding a soluble soap to
the resulting material, and then adding lime
thereto to serve both as an extender or carrier
25 as well as to react with the soap to produce a
water-insoluble water-repellent calcium soap, and
drying the mixture thus produced.

9. The process of producing an improved re-
tarding composition for plasters and the like
30 which comprises treating keratin with an alkali
to hydrolyze the same, incorporating a soluble

soap therewith, adding quicklime to the mixture,
and drying the latter.

10. The process of producing an improved re-
tarding composition for plasters and the like
5 which comprises treating keratin with sodium
hydroxide to hydrolyze the same, incorporating
a water-repellent substance therewith, adding an
extender or carrier thereto, and drying the re-
sulting mixture.

11. The process of producing an improved re-
10 tarding composition for plasters and the like
which comprises treating a vegetable proteid
material containing an oil with an alkali to hy-
drolyze the protein therein and to saponify the
oil to form a soap, thus producing a fluid mix-
15 ture of hydrolyzed protein and soap, adding lime
thereto to form a calcium soap, and drying the
mixture thus produced.

12. A retarder for plasters and the like com-
prising hydrolyzed protein material and a water-
20 repellent substance, said water-repellent sub-
stance being present in amounts in the order of
10% of the protein material.

13. A stabilized set-retarding composition com-
prising a hydrolyzed protein, an inert extender
25 or carrier therefor, and a water-insoluble water-
repellent soap, the ratio of the amounts of said
protein to said soap in the composition being of
the order of 9 to 1.

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