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BONDED PLASTER OF PARIS PRODUCTS AND METHODS OF MAKING SAME

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This application is a continuation-in-part of my co-pending application Serial No. 686,283, filed September 26, 1957, and now abandoned.

This invention relates to new and useful compositions and products, a major ingredient of which is plaster of Paris. These products are useful in the field of orthopedic surgery to make casts or splints to provide immobilization and support for various parts of the human or animal body. However, they may be used for various other purposes such, for example, as to produce molds or forms of ornamental or functional objects.

The plaster of Paris bandages widely used by orthopedic surgeons and others, comprise powered plaster of Paris coated on gauze or other flexible backing material, and bonded together and to the backing by an adhesive. Adequate such bonding holds the coating to the backing not only while the bandage is handled before use but also prevents excessive loss of plaster when the roll or strip of bandage is dipped in water and the excess water squeezed out at the point of use. The usual method of making such a bandage is to coat the backing with a slurry of plaster in a liquid like a volatile alcohol or strong acetic acid, or in water containing a decomposable plaster set inhibitor so that the plaster will not hydrate and become set during the course of manufacture, but will set normally in the finished product. The so coated backing is then dried in an oven or dryer in order to remove the liquid used in the slurry. The binder is usually contained in the slurry, together with materials to control the setting-time of the finished product. For the latter purpose one usually uses powdered potassium sulfate or freshly ground gypsum or mixtures of the two to hasten the set, or sodium or potassium citrate to slow the set. A more stable setting-time can be achieved by using a combination of accelerators and retarders of the setting-time. If a water-insoluble binder is used, it will tend to be more effective than a readily soluble binder, in preventing excessive loss from the wet bandage. At the same time the presence of a water-insoluble binder may seriously interfere with thorough and rapid wetting of the bandage at the point of use, especially if the binder is also not wettable by water. It is desired that even a moderately tightly wound roll of bandage, 6 to 8 inches in width, and five yards long, be thoroughly wet with water when immersed for a period of not more than 5 to 10 seconds. In order to facilitate wetting, the coating is made discontinuous, but even more important, at least one side of the coating is made of roughened contour so that the roll of bandage will wet from the ends of the roll as well as from the sides. In spite of these devices, it is still essential to avoid interference of the binder with the wetting of the bandage. In the use of a water-insoluble binder that does not soften in water, one must not produce a bandage that is too stiff or harsh especially when wet and the bandage must not be so tightly bonded that it prevents the smoothing out of the plaster when it is wet and the cast is being formed. If, however, the surface of the bandage is too soft or slippery when wet, the roll may telescope.

This invention will disclose new and useful products having the required properties as described above and new methods of making such products.

As shown in my co-pending application Serial No. 686,283, filed September 26, 1957, for Plaster of Paris

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Products (expressly abandoned as of December 5, 1962, in favor of continuations-in-part). I have found that the set of plaster of Paris may be delayed for up to several days in contact with an aqueous solution of casein in ammonia, and when heated the water is removed from a mixture or slurry of powdered plaster of Paris in such a solution, the ammonium caseinate is hydrolyzed, the ammonia is removed and the casein remaining, being essentially insoluble in water, does not substantially delay the set of the plaster when the final product is wet in water preparatory to use. The temperature and time required to dry the slurry will depend upon the characteristics of the drier used and in general the temperature may be above about 90° C. (above which temperature plaster of Paris can no longer hydrate with water at atmospheric pressure) and up to about 250° F. However, the drying is not critical except that the heating should not be at so high a temperature and for so long a time as to yield substantial proportions of anhydrite since anhydrite is often very slow to hydrate in use to make a cast. At the same time the casein serves to bond together the plaster of Paris and to bond it to a flexible backing material, such as gauze, when present; and, while the remaining casein is essentially insoluble in water, it is still wettable by water and does not interfere with rapid wetting of the plaster.

Casein contains weakly acid groups (presumably amino-acid groups of somewhat varying acid strength) and when dissolved in aqueous ammonia, it presumably exists in solution as ammonium caseinate. Since ammonium caseinate is the salt of a weak base and a still weaker acid, the salt is subject to appreciable hydrolysis, especially in dilute solution, and an excess of ammonia is required to lessen the degree of such hydrolysis and thus increase the caseinate ion concentration. However, since the equivalent weight of casein is high (presumably over 1000) the relative weight of NH₃ required to dissolve it is small, about 2 to 3 percent of the weight of casein, depending upon the dilution.

Table 1 shows data obtained by adding various small amounts of NH₃ to 100 ml. of water and 0.3125 g. casein (undegraded, dry casein obtained by adding acid to skim milk whereby the insoluble casein acid is precipitated and afterwards washed with pure water and dried at a low temperature—a product known in commerce, for example, as “Argentina Acid Casein”).

Table 1

[0.3125 g. casein and 100 ml. H₂O]

NH ₃ , g.	pH	Plaster Setting-Time
(Pure Water)-----	6.9	6 min.
0.0017-----	7.0	9 m. 30 s.
.0043-----	7.7	9 m. 50 s.
.0051-----	7.8	
.0068-----	7.9	
.0085-----	9.0	11 m. 30 s.
.017-----	9.3	15 m. 30 s.
.034-----	9.9	35 m. 50 s.
.051-----	10.0	37 m. 40 s.
.156-----	10.0	44 m.
.313-----	10.1	43 m. 35 s.

In the experiment of Table 1, the casein remained incompletely dissolved until an amount of NH₃ between 2 and 2.7 percent of the weight of casein had been added and the pH of the solution had reached between 8 and 9. The third column in Table 1 shows the setting-time of plaster of Paris in contact with the corresponding solution. Thus, even after all the casein had dissolved, the setting-time increased in NH₃ until the NH₃ reached from about 16 to 50 percent of the weight of casein. This suggests that the delay (inhibition) is due to the caseinate ion in the solution which is increasing as the

NH_3 concentration increases, since it is known that NH_3 alone does not appreciably delay the set until its concentration reaches 4 to 8 percent.

As the concentration of dissolved casein is increased, with corresponding increase in the NH_3 concentration, the retarding of the set can be increased up to several days. If there is included in the solution plaster set accelerators like K_2SO_4 , ZnSO_4 or freshly ground, "active," finely-divided gypsum (the latter being made by setting plaster with water to form gypsum and drying and grinding the product), the delay in the set will be lessened. Such accelerators are used either alone or in combination in amounts from 0.5 to 3 percent of the weight of plaster. For example, a solution which contains 0.6 percent casein, 0.07 percent NH_3 and an amount of K_2SO_4 equal to 2 percent of the weight of plaster, will delay the set to about 2½ hours; while a solution containing 0.73 percent casein, 2.6 percent NH_3 and an amount of K_2SO_4 equal to 2 percent of the weight of plaster, will delay the set for over 10 hours. A solution containing 0.75 percent casein, 0.09 percent NH_3 and 1.5 percent K_2SO_4 delays the set for several days. It should be pointed out that determination of the setting-time of plaster, especially in such solutions, cannot usually be compared or determined with great accuracy since the setting-time depends to some extent on the inherent properties of the plaster (for example, accidental presence of gypsum of varying degrees of activity in its influence on the set), on whether the slurry is disturbed or stirred, on temperature and on the presence or absence of other dissolved materials such as are commonly used, for example, starch or dextrin binders.

While I may use a solution containing from 0.2 percent dissolved casein up to 3 percent casein and an amount of NH_3 from 2.5 percent of the weight of the casein up to 3 percent of the weight of solution, I prefer to use from 0.5 to 0.8 percent casein and 0.07 to 3 percent NH_3 based on the weight of solution. Highly successful pilot plant runs have been made using an aqueous solution containing 0.7 percent dissolved casein, 2.4 percent NH_3 and additional binders comprising 1 percent cooked corn starch and 1 percent dextrin and a plaster accelerator comprising 0.5 to 1.5 percent K_2SO_4 (the latter three materials weights being based on the weight of plaster used). This corresponds to 0.33 percent casein, 1.1 percent NH_3 , 1 percent cooked corn starch, 1 percent dextrin and 0.5 to 1.5 percent K_2SO_4 —all based on the weight of plaster used. The delay of the set can be adjusted by varying the concentrations of casein and NH_3 in the solution as may be required for a continuous process where the set delay need be only minimal or for a batch process where the slurry may be held for several hours before use.

As additional binders, I use from 0.5 to 3.0 percent (based on the weight of plaster) of corn, white potato, tapioca or other starch, which is cooked, for example, by steaming for about 1½ hours in not over about 12 percent aqueous solution; or dextrin, or an aqueous dispersion of polyvinyl acetate or mixtures of these, for example 1 percent starch plus 1 percent dextrin or 0.75 percent starch plus 1.25 percent dextrin, etc. I may also use methyl cellulose as a binder and softener in amount of 0.5 to 3 percent of the weight of plaster or I may use 0.25 percent of it merely as a softener combined with other binders.

In using casein as above described, I normally do not wish to degrade it by heating in contact with water or letting it stand over a long period in ammonia solution, especially in strong ammonia, because I find that such degraded casein tends to leave residues which slow the set of my final, dry product. I assume this may be due to the fact that when so degraded (hydrolyzed) the hydrolysis forms acids stronger than those found in undegraded casein and thus their ammonium salts are more difficult to completely hydrolyze in the heating and drying

of the slurry. I prefer, thus, to use freshly prepared ammonium caseinate solution (for example, not over 4 to 5 hours old), preferably dissolved in a minimal concentration of NH_3 and I prefer to use the minimum amount of casein relative to the weight of plaster that will give the required delay of the set.

When I use ZnSO_4 , or its hydrates ($\text{ZnSO}_4 \cdot 6\text{H}_2\text{O}$ or $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$) as set accelerators, I must use a larger proportion of NH_3 since some of the NH_3 combines with zinc ion to form the relatively stable $\text{Zn}(\text{NH}_3)_4^{++}$ complex ion. I find, however, that use of ZnSO_4 is advantageous in my process since, after the slurry is dried the NH_3 has been removed from the complex ion, and when the product is wet in water preparatory to use, the Zn^{++} ion from the ZnSO_4 removes the NH_3 which arises through hydrolysis of traces of ammonium caseinate that may be left in the product and thus the ZnSO_4 results in decomposing the ammonium caseinate with consequent reduction of the effect such traces otherwise would have in delaying the set of the product as it is used. Other set accelerators having similar action are the sulfates of other metals which form similar complex ammonia ions such as CdSO_4 , CuSO_4 , CoSO_4 and NiSO_4 .

The plaster set accelerators mentioned may be included in the aqueous slurry or they may be sprayed in the form of fine powder on the dry, finished product. The latter procedure is particularly advantageous when finely-divided active gypsum is used as set accelerator since only a few tenths of a percent is effective and since active gypsum tends to lose some of its effectiveness as a set accelerator when exposed to warm, moist conditions (even to warm, moist air) in the aqueous slurry. Alternatively, I may apply the set accelerator to the dry, finished product in the form of a slurry in a water-soluble material which does not itself affect the set of the plaster. A particularly desirable such material is a liquid or solid polyethylene glycol of relatively low molecular weight such, for example, as "Carbowax." If the such material used is a solid at room temperature, a slurry of the set accelerator may be made in the melted material and sprayed on or otherwise coated in this state upon the dry finished plaster product.

In place of NH_3 , I may use morpholine or a volatile organic amine compound of the general formula



where N is nitrogen and any or all of R_1 , R_2 and R_3 are hydrogen, methyl or ethyl groups. In place of casein, other compounds can be used which are soluble in aqueous NH_3 and contain amino acid groups such, for example, as amino acetic acid, amino propionic acid and the hydrolysis or degradation products of proteinaceous materials commonly called protein hydrolysates, the acid ionization constants of which are in the range of 10^{-7} to 10^{-9} .

My ammonium caseinate set retarder can also be used in a slurry liquid containing methyl, ethyl, propyl or isopropyl alcohol and enough water to dissolve minor amounts of the ammonium caseinate from about 1.5 percent down to about 0.02 percent of the weight of plaster of Paris. This permits a considerable proportion of water in the solution, which will yield a denser final product than is obtained when the slurry solvent is strong alcohol containing only 5 to 10 percent water; and the quantity of ammonium caseinate to sufficiently retard the plaster set, say in 40 percent aqueous alcohol is minimal in relation to the plaster. Another advantage of using a large proportion of water in an alcohol slurry liquid is to permit solution therein of plaster binders like starch, dextrin and methyl cellulose. For example an aqueous solution containing 40 percent isopropyl alcohol sets a plaster containing 1 percent potassium sulfate in about 33 minutes but if the 40 percent alcohol contains 0.07 percent casein and 0.13 percent NH_3 the set is delayed to

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about 56 minutes. The casein in this experiment amounted to 0.016 percent by weight of the plaster of Paris used and the NH_3 about 0.03 percent of the plaster. I find in the case of alcohol-water solutions a larger proportion of NH_3 relative to casein is desirable, presumably due to less ionization to yield caseinate ion in such solutions and I prefer to use an amount of NH_3 from 3 times down to at least equal the weight of casein used.

It will be understood that my aqueous plaster of Paris slurry may be spread upon a gauze or crinoline and dried thereon, or other type of flexible water-wettable backing material may be used. I may also use various types of plaster of Paris including a heat calcined gypsum or a higher density plaster of Paris made by steam-calcining gypsum to form the so-called alpha-gypsum.

What I claim is:

1. The process for making a settable, dry, bonded plaster of Paris product which comprises making a slurry of powdered plaster of Paris in an aqueous solution containing from 0.2 to 3 percent of undegraded casein dissolved in an amount of NH_3 of from at least 0.07 percent up to 3 percent of the weight of solution, forming the desired plaster of Paris product from said slurry while the casein- NH_3 solution acts to retard the setting of said slurry; and then heating said slurry at a temperature between about 90°C . and 250°F . sufficient to remove water and NH_3 therefrom to yield a dry, unset plaster of Paris product wherein no substantial proportion of said casein is left in the form of its ammonium salt and the setting-time of said product is not substantially delayed.

2. The process of claim 1 in which to the said aqueous solution is added from 0.5 to 3 percent of the weight of plaster of Paris of a bonding material selected from the class consisting of cooked starch, dextrine, methyl cellulose, polyvinyl acetate in aqueous dispersion and mixtures thereof.

3. The process of claim 2 to the said aqueous solution of which is further added a plaster set accelerator selected from the class consisting of potassium sulfate in the proportion of from 0.5 to 3 percent of the weight of said plaster of Paris, ground active gypsum in the proportion of a few tenths of 1 percent of the weight of said plaster of Paris and mixtures thereof.

4. A settable plaster of Paris mix comprising a major proportion of powdered plaster of Paris and a minor proportion, substantially 0.2 to 3 percent of the weight of plaster of Paris, of ammonium caseinate retarder for said mix said ammonium caseinate being formed from undegraded casein.

5. A process for making a settable, dry plaster of Paris product comprising in succession the steps; of providing a composition comprising a plaster of Paris mix, a total of from about 0.2 to about 3 percent by weight of said plaster of Paris of the ammonium salt of a material selected from the group consisting of amino acetic acid, amino propionic acid and protein hydrolysates having acid ionization constants of from 10^{-7} to 10^{-9} ; of forming the desired plaster of Paris product in the presence of water while the ammonium salt of said material retards the setting-time of said composition, and of heating said mix at a temperature sufficiently high to cause hydrolysis of said ammonium salt and to evaporate NH_3 and water to yield a dry, settable product whose setting-time is substantially undelayed.

6. The process of claim 1 in which the NH_3 is replaced by at least one nitrogen compound having the formula



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where N is nitrogen and R_1 , R_2 and R_3 are selected from the class consisting of hydrogen, methyl and ethyl groups.

7. The process of claim 5 in which the said ammonium salt of the said material selected is replaced by the salt formed by the reaction of said material selected with at least one nitrogen compound having the formula



where N is nitrogen and R_1 , R_2 and R_3 are selected from the class consisting of hydrogen, methyl and ethyl groups.

8. A settable, dry plaster of Paris bandage comprising a flexible backing material coated with a substantially unretarded, settable, dry plaster of Paris mix comprising in combination: 100 parts by weight of plaster of Paris and a minor amount corresponding to about 0.2 to 3 parts of substantially undegraded casein.

9. The product of claim 8 wherein the casein is replaced by a material selected from the class consisting of amino acetic acid, amino propionic acid and protein hydrolysates having acid ionization constants of from 10^{-7} to 10^{-9} .

10. The process of claim 2 wherein said starch has been steam-cooked at substantially atmospheric pressure in not more than about 12 percent by weight aqueous solution for about $1\frac{1}{2}$ hours.

11. The process of claim 1 wherein the said aqueous solution is freshly prepared and used in said process within 5 hours of its preparation and wherein the amount of the said NH_3 used is from 0.07 to 3 percent of the weight of said solution.

12. The method of claim 1 where said aqueous solution also contains a liquid selected from the class consisting of methyl alcohol, ethyl alcohol, propyl alcohol and isopropyl alcohol and the amount of casein dissolved in said aqueous solution as ammonium caseinate is from 0.02 to 1.5 percent of the weight of plaster of Paris and the NH_3 therein is in an amount from about equal to the weight of the said casein to an amount about 3 times the weight of said casein.

13. The product of claim 8 to which is added a set-accelerator selected from the class consisting of potassium sulfate in amount from 0.5 to 3 percent of the weight of said plaster of Paris and ground active gypsum in amount of a few tenths of 1 percent of the weight of said plaster of Paris.

14. The product of claim 13 to which is added from 0.5 to 3 percent of the weight of said plaster of Paris of a bonding material selected from the class consisting of cooked starch, dextrine, methyl cellulose, polyvinyl acetate in aqueous dispersion and mixtures thereof.

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TOBIAS E. LEVOW, *Primary Examiner*.