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MANUFACTURE OF CASEIN PRODUCTS

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This invention relates generally to the manu-
facture of casein products useful in the paper,
paint, glue and other industries, and more par-
ticularly to casein products containing, in addi-
tion to the usual ingredients, an alkali-metal
metaphosphate such, for example, as sodium
metaphosphate.

Casein has in recent years made an increas-
ingly important place for itself in several in-
dustries. Especially noteworthy are its uses in
the paper, paint and glue industries. In all
of these fields certain properties of the casein
containing mixtures have been serious hin-
drances to the far more widespread adoption and
use of this material. I have found that the
admixture of an alkali-metal metaphosphate
with such casein products overcomes to a great
extent all of the previous disadvantages of such
mixtures.

The alkali-metal metaphosphate which I pre-
fer to use in the preparation of casein products
is the soluble sodium metaphosphate sometimes
called "Graham's salt" which may or may not
have mixed with it a small amount of sodium
pyrophosphate to counteract the slight acidity
of the sodium metaphosphate. There may also
be mixed with the sodium metaphosphate or the
mixture of sodium metaphosphate and pyro-
phosphate, small quantities of alkalis such, for
example, as sodium carbonate, sodium bicarbon-
ate, borax, tri-sodium phosphate and sodium
metasilicate, these alkalis also being added for
the purpose of counteracting the slight acidity
of the sodium metaphosphate. Graham's salt is
believed to consist principally of sodium hexa-
metaphosphate and may be prepared by strongly
heating monosodium dihydrogen orthophos-
phate, and rapidly cooling the molten mass.

In the paper industry casein products are
used either as coating compositions, by which
is meant compositions which are applied to the
paper to give the desired finish thereto, or as
sizing compositions, by which is meant composi-
tions which are applied to the fibers or pulp for
the purpose of acting as a binding agent for the
fibers. Casein compositions are also used in
the finishing or sizing of textiles and in the
sizing of porous surfaces, roofing compositions
and the like. My invention will be described
herein as applied particularly to the coating
of paper, it being understood, however, that the
invention is not restricted to this particular use,
but may be used for other purposes for which
casein products are fitted.

The method now generally used for preparing

coating mixtures for paper is to soak the dry
casein in water for a sufficient length of time
to moisten each particle thoroughly before add-
ing the solubilizing agent. After the casein is
soaked an alkali is added thereto. This is gen-
erally done by dissolving the alkali in a small
amount of water and pouring the solution into
the vessel which contains the casein. Various
alkali solubilizing agents have been used, among
which may be mentioned sodium silicate, sodium
aluminate, sodium phosphate, sodium carbon-
ate, sodium borate, caustic soda and ammonium
hydroxide. The corresponding potassium salts
may also be used, but their expense makes their
use infeasible. In general, selection of the sol-
vent depends upon the type of paper being made.
Slaked lime has not proved desirable as a solu-
bilizing agent for casein paper coating compo-
sitions, although it has been used with con-
siderable success in the manufacture of casein
glues. Lime, when used in casein paper coat-
ings, has the objection that it reduces the work-
ing life of the coating and seems to increase
greatly the foaming properties of the coating.

There are certain disadvantages common to
all types of casein paper coatings whether or
not such coatings contain lime, among which
are:

1. It is very difficult to control the fluidity of
the casein mixture so as to obtain the proper
results in the coating operation.

2. There is a great tendency for particles of
the casein to remain undissolved, which particles
collect in the brushes used in applying the coat-
ing and from which they drop off onto the paper,
forming lumps thereon.

3. The property of foaming is pronounced in
all paper casein coatings and is especially evi-
dent in those coatings containing lime.

I have found that the addition of an alkali-
metal metaphosphate to such coatings whether
or not they contain lime greatly decreases or
completely overcomes the objections to such coat-
ings as are now in use.

In describing my invention I will confine my-
self to the use of the preferred alkali-metal
metaphosphate, namely, sodium metaphosphate,
but it is to be understood that other alkali-metal
metaphosphates such, for example, as potassium
metaphosphate, lithium metaphosphate, and am-
monium metaphosphate may be used. All of
these metaphosphates are preferably used in
the soluble form commonly known as hexameta-
phosphate.

In the preparation of lime-containing casein

coatings I have used the following proportions of ingredients:

	Parts by weight
Casein -----	100
5 Lime -----	20-30
Sodium metaphosphate -----	20-125

The working life of the coating is roughly proportional to the amount of sodium metaphosphate added. By "working life" is meant the period of time during which the coating may be worked. It is the period of time from the time at which the coating was made to the time at which it solidifies or sets or becomes so viscous that it is unsuitable for the intended purpose. If there are added, let us say, 20 parts of sodium metaphosphate, the working life of the coating may be only six hours, whereas if 100 parts are added the working life of the coating is extended to as much as 72 hours. In making the coating the casein is soaked for about an hour in about three times its weight of water, which water contains the desired amount of sodium metaphosphate, the mixture being stirred. Then while stirring the casein metaphosphate solution, the lime dissolved in 100 parts of water is added. The stirring is continued thereafter for about one-half hour and the desired mineral matter is added. The mineral matter may be white clay, precipitated chalk, or other suitable material. The amount of each of these minerals to be added varies from about 5 to 20 parts per 100 parts of casein and depends largely upon the type of coating desired.

I have found that the addition of metaphosphate to casein paper coating is very effective in solving the chief difficulty involved in the use of these coatings, that is, keeping the viscosity of the mixture at such a point that it may be easily applied by the brushes. It likewise reduces the amount of foaming encountered in mixtures of this type.

Although due to the complicated nature of the material involved, the exact reasons for the improvement obtained by employing the sodium metaphosphate are not definitely known, it is believed that the improvements are due to two factors. The first of these is the effect of sodium metaphosphate upon certain metallic ions such as calcium and magnesium. It is known that metallic salts of casein such as calcium caseinate and magnesium caseinate are highly insoluble and are formed very rapidly whenever casein is mixed with calcium or magnesium-containing compounds. Sodium metaphosphate reduces considerably the concentration of such metal ions when it is mixed with them in solution. It is believed that the action of the sodium metaphosphate is to sequester or lock up the calcium or magnesium in a but extremely slightly ionized condition in a soluble sodium-calcium-metaphosphate complex molecule or the corresponding sodium-magnesium-metaphosphate complex molecule. The action of the metaphosphate prevents the rapid formation of the insoluble casein salts of calcium and magnesium, thus keeping the casein mixture for comparatively lengthy periods of time from getting so thick that it cannot be worked easily.

There is, however, another effect of the sodium metaphosphate which appears to be entirely apart from its action upon calcium and magnesium. This effect is the solubilizing action of the sodium metaphosphate on casein and is illustrated by the following example.

Example I

Two mixtures were made, the first containing one gram of casein in 100 mls. of a 2% solution of sodium chloride and the second containing one gram of casein in a 2% solution of sodium metaphosphate. The pH values of each of the mixtures was the same, about 5.8. Upon shaking each solution the one containing sodium metaphosphate yielded a stable foam, whereas the one containing sodium chloride did not, thus demonstrating that the sodium metaphosphate solution had a specific solubilizing effect upon the casein which could not be attributed either to salt concentration or pH, which were the same in both cases. Each solution was then filtered. To 25 mls. of each of the filtrates were added 25 mls. of a special oil known to the trade as "Olive Elaine", this oil being a purified oleic acid and the mixtures were shaken. The sodium chloride-casein-oil mixture formed no emulsion whatever. Immediate separation of the original light yellow-colored oil took place. In the case of the sodium metaphosphate-casein-oil mixture an emulsion was formed which, after a few moments, separated into two layers, neither one of which looked like the layers of the sodium chloride-casein-oil mixture. The upper layer of the sodium metaphosphate-casein-oil mixture was very white and opaque and was probably a concentrated water and oil emulsion. Although the lower layer of this mixture was not as opalescent as the upper layer, it was considerably more opalescent than the lower layer in the sodium chloride-casein-oil mixture. In the case of the sodium chloride-casein-oil mixture the upper layer was, as far as could be ascertained visually, pure oil with no sign of an emulsion.

Since in making the two mixtures pure salts were used, the pH of the mixtures were very close to that of distilled water, and the emulsion obtained with the metaphosphate-casein-oil mixture was undoubtedly due to a specific solubilizing effect of the sodium metaphosphate upon the casein. After a period of 24 hours the appearance of the metaphosphate-casein-oil emulsion was the same. In other words, a stable emulsion had been formed and there was no further separation in 24 hours.

Example II

In this example a mixture was made by adding casein in excess to 100 mls. of 10% sodium metaphosphate solution, shaking the solution and filtering it. To 25 mls. of this filtrate were added 25 mls. of the "Olive Elaine" referred to in Example I, the mixture was shaken vigorously, and 25 mls. of this mixture were put into a 25 ml. graduate. A second mixture was made following the same procedure but using sodium chloride instead of sodium metaphosphate. In making the second mixture casein in excess was added to 100 mls. of 10% sodium chloride solution and the mixture shaken and then filtered. To 25 mls. of this filtrate were added 25 mls. of the above-mentioned "Olive Elaine", the mixture was shaken vigorously, and 25 mls. of the mixture was put into a 25 ml. graduate. The sodium chloride-casein-oil mixture broke immediately into two layers of which the volume of the upper creamy layer was 16 mls. and the lower water layer 9 mls. In the case of the sodium metaphosphate-casein-oil mixture there was no breaking up of the emulsion. In six hours the sodium chloride-casein-oil emulsion had broken down completely

into 13 mls. of oil and 12 mls. of water, while in the same length of time the sodium metaphosphate-casein-oil mixture contained 16½ mls. of a creamy emulsion and 8½ mls. of water.

Twenty-four hours later the sodium chloride-casein-oil mixture was clearly divided into the original mixture of 50% oil and 50% water, while the sodium metaphosphate-casein-oil mixture divided into 16 parts of a creamy emulsion and 9 parts of water. About 5 hours after this observation it was noted that the creamy emulsion of the sodium metaphosphate-casein-oil mixture had solidified.

This example shows definitely that sodium metaphosphate has some peculiar effect upon casein which cannot be attributed purely to salt effect. The mixture of casein and sodium chloride prepared as above described had very little power toward the emulsification of the oil. The mixture of sodium metaphosphate and casein, on the other hand, made a very stable emulsion; in fact, a solid emulsion under exactly the same conditions. Since the mixture of casein and sodium chloride did not emulsify the oil, and since it is known that sodium metaphosphate by itself does not have pronounced emulsifying properties on oil, it follows that there can be only one explanation of the very stable emulsion which the sodium metaphosphate and casein formed with the oil, and that explanation is that the sodium metaphosphate and casein mixture exhibits entirely different properties when used for emulsifying oil or other oleaginous material than either the sodium metaphosphate or the casein exhibit separately. It is believed that due to the solubilizing effect of the sodium metaphosphate on the casein a solution is formed which acts as an emulsifying agent for the oil.

Example III

In this example four mixtures were made as follows. The first sample or mixture contained 100 grams of casein. The second mixture contained 100 grams of casein and 25 grams of sodium chloride. The third mixture contained 100 grams of casein and 25 grams of sodium metaphosphate. The fourth mixture contained 100 grams of casein and 25 grams of "adjusted" sodium metaphosphate. The "adjusted" sodium metaphosphate referred to in mixture four consisted of sodium metaphosphate containing about 10% sodium pyrophosphate, about 4% of soda ash and 2% of sodium bicarbonate, these last named ingredients being used for the purpose of adjusting or increasing slightly the alkalinity of the sodium metaphosphate.

To each of the four mixtures were added 500 mls. of water, the water being added in five portions of 100 mls. each. Each of the mixtures was stirred vigorously and let stand for one-half hour in bottles of the same diameter and height. At the end of that time the percentage of settling out of the casein was calculated by dividing the height of the clear top liquor by the total height of the mixture. The results were as follows: Neither mixture three nor mixture four showed any settling out of the casein whatsoever. These were the two mixtures containing, respectively, casein and sodium metaphosphate, and casein and "adjusted" sodium metaphosphate. Mixture two, which contained casein and sodium chloride, showed 22% settling; and mixture one, which consisted of casein only and water showed 28% of settling.

Although there was no settling in either of the mixtures three or four, mixture four, containing the "adjusted" sodium metaphosphate, was very viscous and stiff. This was undoubtedly due to the fact that the pH of this particular mixture was a little higher than the pH of the other mixtures, which were about 5.5. Mixture three, containing the ordinary or "unadjusted" sodium metaphosphate was very much less viscous.

This example again shows definitely that sodium metaphosphate has a specific solubilizing effect upon casein which cannot be attributed either to salt concentration or to the pH value of the solution.

Casein paints

My invention is applicable to the production of casein paints. Casein paints as now generally produced are made by mixing casein and an alkali such, for example, as lime, together with whiting, clay, or other paint pigments, and a preservative such as borax. In general, the amount of casein used is approximately 15%, the amount of lime, if that is the alkali which is employed, is about 15%, and the remainder of the composition is made up by the other paint pigments, fillers and coloring pigments. It will be understood that these percentages vary greatly according to the particular type of paint. The working life of such casein paints is extremely short. Calcium caseinate is formed almost immediately upon mixing with water and the resulting paint becomes so thick that it cannot be used.

I have found that by adding sodium metaphosphate to casein paint in approximately the same proportions as were mentioned in connection with the preparation of casein paper coatings I am able to prolong the working life of the paint considerably, in some cases for as long a period as 96 hours. Another advantage in the use of sodium metaphosphate in casein paints is that it enables one to add water at any time during the working life of the paint to allow for such evaporation as has taken place. This is a decided advantage as it is recognized that casein paints heretofore known cannot be diluted after they have once been prepared. The amount of sodium metaphosphate or other alkali-metal metaphosphate added depends largely upon the length of working life desired for the paint. The amount of sodium metaphosphate added may vary from a very small quantity which will not have a pronounced effect upon the length of the working life of the paint to a considerable amount which will have a very marked effect thereon.

Casein glues

My invention is applicable also to the production of casein glues and other adhesives. The excellent properties of casein glues have been known for a long time. Casein glues containing lime have been used for many years in the preparation of water-proof joints since calcium caseinate is a highly insoluble salt. A serious failing of this type of glue is, however, that its working life is so short as to necessitate making it up in very small quantities, with the subsequent waste involved.

I have found that by adding an alkali-metal metaphosphate such as sodium metaphosphate to such casein glues, the working life thereof can be markedly increased without affecting ad-

versely the adhesive properties of the glue. A glue may be prepared, for example, as follows:

Example IV

- 5 200 grams of casein, 200 grams of sodium metaphosphate and 100 grams of calcium hydroxide were added, with stirring, to 600 mls. of water. During the next 15 minutes an additional 600 mls. of water was added to the mixture and stirring was continued for one-half hour. A white homogeneous mixture was obtained which had a working life of 96 hours and exhibited excellent adhesive properties.

Example V

- 15 In this example the same mixture as given in Example IV was prepared and there was added to that mixture, with stirring, copper sulphate in the amount of five grams dissolved in 50 mls. of water. The resulting glue had a working life of about 80 hours. The copper sulphate was added for the purpose of increasing the water resistance of the glue. Heavy metal salts of casein such as copper caseinate are very insoluble and increase markedly the water-proof properties of the glue. Other heavy metal salts such as soluble salts of zinc, lead, tin, etc., may be used in place of the copper sulphate if desired. Heretofore after the addition of such a salt to a casein glue, it was necessary to use the glue up immediately since hardening took place very rapidly. By using sodium metaphosphate I have been able to make casein glues having very high resistance to water and with a working life of 75 to 100 hours. The working life of the glue depends largely upon the amount of alkali-metal metaphosphate added.

- The alkali-metal metaphosphate employed in accordance with the present invention in the production of casein products is effective in improving not only such products as contain lime and magnesium, but also such products as do not contain them. The alkali-metal metaphosphate is particularly effective in casein products containing lime or magnesium for the reason, it is believed, that in addition to the specific solubilizing effect of the metaphosphate on the casein, there is the additional effect of the metaphosphate on the lime or magnesium by which they are sequestered or locked up in a but extremely slightly ionized condition in a soluble sodium calcium metaphosphate complex molecule or a soluble sodium magnesium metaphosphate complex molecule.

Other alkalies than lime may be used as the solubilizing agent for the casein whether the product is to be used as a coating or sizing agent, paint, glue or other composition. For example, caustic soda or other alkali may be used in place of lime where heavy metal salts are employed in the manufacture of casein glue.

I have described in detail certain preferred procedures and have given certain specific examples. It will be understood, however, that the invention is not limited to the examples or procedure described, but may be otherwise embodied or practiced within the scope of the following claims.

I claim:

1. A plastic setting mass adapted for use as coating and sizing compositions, paints, glues and the like, containing casein, an alkaline earth metal, and an alkali-metal metaphosphate.
2. A plastic setting mass adapted for use as coating and sizing compositions, paints, glues and the like, containing casein, an alkaline earth metal, an alkali-metal metaphosphate and mineral matter.
3. A plastic setting mass adapted for use as coating and sizing compositions, paints, glues and the like, containing casein, lime, an alkali-metal metaphosphate and mineral matter.
4. The process of emulsifying casein-water-oleaginous mixtures, which comprises mixing therewith an alkali-metal metaphosphate.
5. The process of emulsifying casein-water-oleaginous mixtures, which comprises mixing therewith sodium metaphosphate.
6. A plastic setting mass adapted for use as coating and sizing compositions, paints, glues and the like containing casein, a solubilizing agent for casein, and an alkali-metal metaphosphate.
7. A plastic setting mass adapted for use as coating and sizing compositions, paints, glues and the like containing casein, lime, and an alkali-metal metaphosphate.
8. A plastic setting mass adapted for use as coating and sizing compositions, paints, glues and the like containing casein, a solubilizing agent for casein, a heavy metal salt, and an alkali-metal metaphosphate.
9. A plastic setting mass adapted for use as coating and sizing compositions, paints, glues and the like, containing casein and an alkali-metal metaphosphate.

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