**Title:** COATING METHOD FOR ENCAPSULATION OF PARTICULATE MATTER

**Abstract**

Particulate and fibrous materials are encapsulated with a monolithic coating of controlled thickness, by treating the particulate material with a phosphate liquid and an alkali-metal or alkaline-earth metal compound which reacts with the phosphate liquid to form a wet phosphate paste which subsequently hardens. This may be done in a granulator drum or spraying process. Deposition of an excess amount of phosphate solution on the particulate surfaces leads to bonding of the encapsulated products. The process can be repeated until the desired coating thickness is achieved.
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COATING METHOD FOR ENCAPSULATION
OF PARTICULATE MATTER

TECHNICAL FIELD OF THE INVENTION

This invention relates to the deposition of a cementitious monolythic coating on particulate matter of diverse origin.

BACKGROUND OF THE INVENTION

Several particulate material types could substantially benefit from surface protection as provided by encapsulation. Some particulates are porous (such as vermiculite or expanded perlite), hygroscopic (such as potash, ammonium nitrate and urea among others), flammable (polystyrene beads and wood fibers) or fragile (mineral wools, glass fiber or asbestos) and require some means of surface stabilization to impart properties such as a sealed surface, moisture resistance, some degree of fire retardancy and improved mechanical strength, respectively. Pelletized or granulated nuclear waste materials could be safely transported by remote pneumatic means if they could be solidly encapsulated to avoid radioactive contamination of pipes and pumping equipment used in the transfer process.

In a well designed encapsulation method, the size of the particulates to be protected can be immaterial and the mean particle diameter may range from 5 microns to as large as several centimeters.
In the past, encapsulation has been readily obtained by slurring the particulate material in a suitable coating material such as varnish, paint, rubber, various plastics, molten sulphur and even molten glass and metals. However, such coatings are not universally usable, neither are they always waterproof or rigid enough nor do they have the required weathering and fire resistance as required in diverse applications.

Other technologies described in the prior art are cumbersome, and in most cases require special procedures and equipment for application of protective coatings to particulate materials; furthermore, several of these processes employ endothermic reactions, necessitating the expenditure of additional energy. Oftentimes the granular material itself is quite soluble in phosphoric acid and water, and thus when such materials are used, significant losses in substrate volume are encountered on extensive mixing before the coating gets established and all of the moisture is removed. The known procedures of this type involve mixing solutions of highly concentrated (50%-95%) phosphoric acid with the particulate material, as is shown in Christoffel et al. (U.S. Pat. No. 3,392,007), this being followed by an application of magnesium oxide powder to neutralize the acid in the coating and the addition of ammonium phosphate at elevated temperatures (e.g., 80°C) to obtain a hard, water-resistant coating of the magnesium ammonium
phosphate type, this coating representing some 25-60% by weight of the product.

Salutsky et al. (U.S. Pat. No. 3,285,731) show a process for co-granulation of magnesium and potassium containing phosphates to improve their non-burning nutrient qualities and control the release of nutrients to plants when applied as a mixed fertilizer. This co-granulated product is made by mixing magnesium ammonium phosphate with 1-99% by weight of magnesium potassium phosphate (and optionally trace elements with them in the phosphate form) in a granulater or by co-precipitation from respective salt solutions and granulation of the precipitated solids. Stevenson (U.K. Pat. No. 1,135,778) show the manufacture of granulated magnesium ammonium phosphate fertilizer by mixing magnesite and monoammonium orthophosphate in the presence of water at elevated temperatures to obtain a slow release coated fertilizer.

Goodale et al. (U.S. Pat. No. 3,419,379) shows a coating for ammonium nitrate (NH₄NO₃) granules in which the granules were first coated with an acidic super phosphoric acid (H₃PO₄) or oleum. The wet granules were then contacted with basic materials such as NH₃, MgO, or CaO. The reaction product of the acid with the basic material produced a coating around the granules which prevented them from caking and retarded their dissolution on contact with moist soil. Japanese Pat. No. 8,105,393 to Japan Kokai Tokkyo Koho describes encapsulation of urea with a resin
and hexaoxyethylenenonylphenyl ether (1%) surfactant to impart water insolubility to the fertilizer particles. Blouin (U.S. Pat. No. 3,991,225) describes a process for producing sulphur-coated urea. Mueller (U.S. Pat. No. 4,023,955) shows controlled release fertilizer formulations which were prepared by first coating the fertilizer granules with a hydraulic cementitious mixture followed by a thin semi-permeable elastomeric coating of the styrene butadiene acrylic type and a third, partially hydrated homogenous cement fertilizer mixture containing micronutrients. In this case, the cement coatings were of the masonry and portland cement types.

Another major disadvantage of the known coatings described above, in addition to the cumbersome and expensive special procedures typically required, is their relative sensitivity to nitrifying bacteria in soils, whereby the otherwise waterproof magnesium ammonium phosphate structure is rapidly attacked and degraded when such fertilizers are applied in the field, with the resultant destruction of the slow-release aspect of the fertilizer coating as it is rapidly lost. The present invention, due to the absence of ammonia linkages in the magnesium oxyphosphate condensate (which will be described below), overcomes this major disadvantage of the known coatings for fertilizer granules.
It has been observed by Limes et al. (Canadian Patent No. 765,874, 1967) that when dead burned magnesite (MgO) was brought into contact with liquid ammonium polyphosphate (10:34:00 or 11:37:00), a rapid exothermic reaction took place which resulted in the formation of a monolithic solid and liberation of ammonia. When the slurry was placed in a mold or pressed, a cementitious solid was obtained which was hard, heavy, insoluble in water, of high dimensional stability, fire resistant and quite strong.

In an invention to Paszner (Canadian Patent No. 1,081,718, 1980) wood particulate material was mixed with ammonium polyphosphate and dead burned magnesium oxide in certain proportions and when the cementitious mixture was allowed to cure, solid products were obtained that had high compressive strength, excellent dimensional stability and fire resistance in spite of the high wood content. The reaction was found to be fast enough so that the mixtures could also be used in spray equipment to produce fire retardant protective spray coatings over large surfaces.

SUMMARY OF THE INVENTION

There now have been invented, and disclosed herein, certain new and novel processes for encapsulating the individual particles of a particulate material which are free of the above-discussed and enumerated drawbacks and disadvantages of currently known coating and encapsulation processes.
These novel processes are suitable for encapsulating particulate materials, including both granular and fibrous materials, and are characterized by the initiation of a reaction on the particulate surfaces by the application of (a) a liquid phosphate and (b) a particulate material capable of reacting with the liquid phosphate to form wet phosphate paste which solidifies upon curing. The particulate material may be, for example, a particulate alkali-metal or alkaline-earth metal compound.

In a preferred embodiment, the particulate material is combined with the liquid phosphate solution in a controlled amount sufficient for forming a film of desired thickness over the particulate material. The wetted particulate material is rapidly mixed with an excess of a cementitious powder mixture containing alkali-metal or alkaline-earth metal oxides, carbonates, chlorides, and/or silicates, this powder being of a sufficiently small size to form a continuous coating on the particulate surfaces. This may be done, for example, in a drum, or by fluidizing the wet particulates in an air stream and combining them in the stream with similarly fluidized cementitious powder mixture. In this latter example, the mixing may be pre-formed in a spraying apparatus, with the proportions being defined by the wetting ability of the phosphate solution film as situated on the particulate material.
The coated particulate material is then agitated, preferably in an excess of the cementitious solids, or separated by floating these particulates in an air stream, until the paste coating which was formed by the reaction of the phosphate solution with the cementitious powder has cured and substantially hardened, and so has lost its surface tackiness. The coated particulate material can then be separated from the excess mineral solids of the cementitious powder mixture by sieving or other processes of segregation. If the particulate material is sensitive to residual moisture in the coating, it may be subsequently dried, as, for example, in a drum dryer or hot air stream, until the excess moisture is driven off.

In those cases where it is desired for the coated particles to be subsequently bonded together, the liquid phosphate solution may be proportioned in a ratio relative to the cementitious solids such that a slight excess of liquid remains available on the particulate surfaces, so that following deposition of the encapsulated particles, subsequent curing will bond the individual particles together to form a continuous matrix.

Examples of suitable alkali-metal or alkaline-earth metal materials may include dead burned magnesite, magnesium oxide heavy powder, calcined dolomite, calcined magnesite, calcined olivine, calcined serpentine, or calcined marble powder. Raw dolomite, magnesite, olivine,
serpentine, and potash will similarly react, albeit at slower reaction rates than the materials listed above, although these reaction rates may be accelerated by heating. As for the liquid phosphate, this may be, for example, ammonium polyphosphate or phosphoric acid of suitable concentrations.

These and other important features of the present invention and additional advantages thereof will be apparent to the reader from the foregoing and the appended claims, and from a reading of the ensuing Detailed Description of the present invention.
DETAILED DESCRIPTION OF THE INVENTION

During the course of the present investigations it was discovered that, depending on the reactivity of the dead burned magnesite and the level of ambient temperature during the magnesium oxyphosphate reaction, when granulated materials were treated with a limited quantity of liquid ammonium polyphosphate or superphosphoric acid (syrupy) and subsequently mixed with a large excess of high reactivity dead burned magnesite or various forms of calcined dolomite and similar magnesium-containing mineral compounds, the phosphate wetted particulate material became coated with a well adhered magnesium oxyphosphate (the reaction product of ammonium polyphosphate and dead burned MgO) to form rounded particles which have sealed surfaces without being glued together. If agitation during the reaction is vigorous enough and the MgO powder is available in large enough excess, the particles do not stick together and can be readily separated from the excess MgO powder by sieving through appropriately grated screens. This procedure could be repeated as many times as desired or required to build up a coating of the desired thickness around the particles.

It was further found that the process of particulate coating can be made continuous if (a) the ammonium polyphosphate-wet material is continuously fed into a drum, placed on a slight incline, containing the MgO powder mixture,
(b) rapidly mixing the ammonium polyphosphate-wet particulates by rolling into the MgO solids until all the free liquid is consumed on the surfaces and the particles become well coated, (c) allowing the coated particles to rest so that the cementitious coating can sufficiently harden, (d) removing the excess MgO powder by sieving or air separation, and (e) allowing the resulting coating to fully cure and lose its excess moisture. In such continuous coating processes it may be desirable to speed up the reaction to increase the throughput. This can be achieved by (1) replacing part of the MgO with calcined dolomite, magnesite, circonia, spent flue gas scrubbing dolomitic limestone, calcined olivine, serpentine or marble powders, (2) by use of chemically pure magnesium oxide heavy powder (Merck Chemicals), (3) by use of syrupy superphosphoric acid, or (4) by use of warm (60–80°C) ammonium polyphosphate or a combination of these options. Heating the MgO solids in the drum bed is a relatively simple way to achieve such elevation in temperature in the reaction mixture as the cement solids are capable of absorbing substantial amounts of heat. Heating the MgO powder and pre-heating the ammonium polyphosphate may be advantageous in some instances where reactivity of a cheaper source of MgO requires additional energy to initiate the exotherm reaction to obtain fast coating speeds. In most cases, however, a combination of MgO sources is sufficient in modifying the reaction speed.
In the case when too much ammonium polyphosphate is applied to the particulate material, "caking" and bonding between the particles may arise following such initial coating.

Alternately, coatings can also be applied to particulates by a combination of dusting and spraying in which case air is used to transport (fluidize) the particles and to keep them detached from each other. Wetting is obtained by spraying the particulate surfaces with finely atomized ammonium polyphosphate. In this case sufficiently high air-to-solids ratios have to be maintained to keep the particles well separated to avoid coalescence of the liquid droplets and to avoid sticking. Once the coating is adhered, the wet particulates are allowed to drop through space and partly supported by countercurrently flowing hot air to speed the curing rate.

When such coated particles contain sufficient excess ammonium polyphosphate and are impacted or deposited on solid surfaces before the reaction (hardening) of the coating is complete, solid continuous coatings of well encapsulated particles will result whereby the processes of particulate encapsulation and bonding are sequential steps and combined in one process.

Thus, features of exemplary processes in accordance with the present invention are as follows:

(a) combining said particulate materials with liquid phosphate solution in an amount
sufficient for forming a thin film over the said particulate material;

(b) rapidly mixing such particulate material with an excess of the reactive cementitious powder mixture of sufficiently small size so as to form a continuous coating on the particulate surfaces either in a drum or in form combining said wet particulates with an air stream to fluidize the aid particulates and combining them with similarly fluidized cementitious mixture in a suitable spraying apparatus in proportions defined by the wetting ability of the free phosphate solution film situated on the particulate material;

(c) transporting and agitating said coated particulate material in an excess of the cementitious solids, or floating them in an air stream, until the particulate coating has essentially and substantially hardened and lost its surface tackiness;

(d) separating such coated particulate material by known processes of segregation, sieving or such as may be advantageous from the excess mineral solids, and

(e) if the particulate material is sensitive to the residual moisture in the coating, it may then be dried by known means as in a drum drier or hot air stream until most of the moisture is driven off.

If the Steps (a) to (b) are carried out in such a way that the MgO containing cementitious solids
and ammonium polyphosphate are proportioned in a ratio so that a slight excess of liquid is available on the particulate surfaces, then on deposition of such encapsulated particles on a solid surface hardening (curing) will take place and a layer of such coated particles is formed on that solid surface in a manner that the said coated particles are also bonded to each other to form a continuous matrix of particles and air pockets, or a continuous matrix without air pockets if the encapsulated particulates are impacted on the surface. The density of such continuous matrices is readily controlled by the speed at which the impact of the coated particles on the surfaces occurs.

The temperature of the reaction medium or the coating components can be controlled in Step (a) as by controlling the temperature of the phosphate solution, in Step (b) by controlling the temperature of the MgO-containing cementitious mixture and in Step (c) by controlling the temperature of the fluidizing medium, e.g., the excess MgO cementitious solids or fluidizing air. Such controlled temperatures may be readily generated by known means of heating and will result in substantially increased reaction rates to solidify the coatings and speed up the loss of surplus moisture (as in Step (e)) and release of ammonia by-product gas.

A partial solubility of the particulate substrate in the liquid phosphate solution during
the coating process does not seem to affect the reaction rate or the hardness of the coating.

A suitable MgO cementitious matrix may be comprised entirely of dead burned or calcined magnesite from mineral or seawater sources, or chemically pure magnesium oxide heavy powder, or may be of magnesium oxide-rich dolomite, up to 99.5% raw ground magnesite, dolomite, zirconia, olivine, serpentine or marble powder or other additives which would at least partially precipitate phosphate from ammonium polyphosphate or superphosphoric acid solutions by reacting with them under certain conditions as determined largely by the stoichiometry of the components and/or the reaction environment (temperature). In particular, it has been found that raw dolomite, olivine, magnesite and serpentine will react without the addition of heat if a minimum amount (generally, at least 3%) highly reactive (calcined or well dead burned) MgO is present. Alternatively, raw ore can be reacted at an elevated temperature without the presence of reactive MgO; in this regard a temperature of about 80°-100°C has been found suitable.

In addition to the MgO-containing cementitious materials described above, there are other suitable compounds available which will react with the liquid phosphate so as to precipitate a curable phosphate paste. These include numerous other alkali-metal and alkaline-earth metal compounds, notably potash (e.g., KCl), as well as other compounds. Potash and MgO-potash
mixtures have been found particularly suitable for use in coating granulated potash and urea fertilizers. Additives other than those described above may be added to the cementitious mixture as required or suggested by the particular application for which the coating is designed without adversely affecting the curing speed of the coating. Such additives may be, for example, magnesium nitrate, potassium chloride or sulfate, lignosulphonic acid, urea, ammonium nitrate, boric acid, iron oxide, ferrous sulfate, ferric chloride or virtually any inorganic solid from a few percent and up to 50 per cent of the cementitious solids. Such additives would be well blended with the MgO containing solids and usually ground to the same extent as the MgO.

EXAMPLE I

About 50 grams of expanded perlite of 1.0 to 5 mm diameter was treated with 75 g of ammonium polyphosphate (10:34:00) of commercial grade (Simplot Chemical Co., California) in a suitable plastic bag. The liquid phosphate was well distributed over the perlite by shaking. To the wet perlite mass about 500 g of dead burned magnesite powder was added in a large plastic bag. The MgO had a particle size passing -200 mesh sieve (National Refractory Chemicals, Moss Landing, California). The perlite-MgO mixture was vigorously tumbled until the particles became well separated and coated with magnesium oxyphosphate.
(MOP) (about 2 minutes). The mixture was allowed to stand for an additional 5 minutes before shaking the bag again and separating the unreacted MgO by using an 80 mesh sieve. Tumbling the coated particles for an additional 3 minutes resulted in "polished" pellets. The loose small powder was removed by sieving again on an 80 mesh sieve and added to the rest for reuse with the next batch.

The total weight increase on the perlite was 112 g of which 18 g was reacted ammonium polyphosphate solids, 77 g was MgO and 18 g was water. About 35 g of the ammonium polyphosphate remained unreacted and absorbed into the perlite pores.

On drying in a forced air oven at 50°C with gentle tumbling in a drum for three days, the coated material lost a total of 36 g of moisture and ammonia which was liberated by the MgO-ammonium polyphosphate reaction.

The procedure was repeated up to 5 times, except that starting with the second coating mixture the amount of ammonium polyphosphate was reduced to 25 g for all subsequent applications.

The average particle diameter after the 5th encapsulation ranged between 3 to 7 mm.

**EXAMPLE II**

The same mixing sequence was followed with the same proportions using perlite as the substrate, as described in Example I with the
exception, that the MgO powder was preheated to
100°C in an oven before combining the phosphate
wet perlite with the cement solids.

In this case the reaction was instantaneous
as indicated by the almost immediate release of
ammonia. The coated material weight was 118 g and
the MgO was 83 g following the second fines
removal by sieving.

EXAMPLE III

To 50 grams of expanded perlite 150 g of
ammonium polyphosphate was added in a plastic bag
to which immediately 150 g of cementitious powder
mix was added. The powder consisted of 30% (50 g)
-200 mesh dead burned MgO (made from sea water by
Kaiser Refractories, Oakland, California) and 70%
of -200 mesh ground garden dolomite. The cement
powder was rapidly shaken with the wet perlite
particles and the resulting mixture was poured
into a dish and allowed to stand for 10 minutes by
which time it hardened into a solid slab of low
density. The encapsulated perlite particles were
bonded together at their contact points. The slab
was dried to 15% moisture in the air in four days
giving off only faint ammonia odor at that stage.
The ammonia odor disappeared within a week or
eight days.
EXAMPLE IV

A series of samples was prepared with the same mixing ratios as in Example I except that the MgO source was replaced by -200 mesh calcined dolomite. The calcined dolomite was prepared by heating garden dolomite (45% MgO content) at 850°C in a muffle furnace for 8 h and on cooling the material was reground to pass 200 mesh.

The calcined-dolomite-to-raw-dolomite-ore ratio was varied between 100% calcined dolomite to 95% raw dolomite (the rest calcined dolomite). The reaction rates with all the mixtures below 70% raw dolomite content were very rapid (almost instantaneous) whereas those of the mixtures having more than 70% raw dolomite were comparable in rate to those had with the dead burned MgO mixtures.

Equally rapid curing (hardening) rates were obtained when a maximum of 15% chemically pure magnesium oxide heavy powder was added to the raw dolomite powder. Heavy powder MgO addition to raw dolomite as low as 0.5% was effective in initiation of the reaction and hardening of the coatings, albeit at somewhat slower rates. Mixtures containing less than 5% MgO heavy powder in raw dolomite cured at the same rate as observed with dead burned MgO mixtures containing less than 50% raw dolomite.
EXAMPLE V

One hundred grams of prilled urea (average diameter 2.5 mm) ammonium nitrate prills or processed potash (KCl) were mixed individually with 35 mL of clear ammonium polyphosphate solution of 11:37:00 (TVA, Muscle Shoals, Alabama) composition in plastic bags. The wet particulates were treated with 500 g of -200 mesh dead burned magnesite-dolomite mixture (30% MgO and 70% dolomite) in plastic bags and rapidly tumbled around to prevent the prills from being glued together by the MOP matrix. After mixing for 2.5 minutes the prills were well separated and encapsulated with MOP coating. The coating thickness was about 0.4 to 0.7 mm with average prill diameter of about 3.5 mm for the urea prills.

Trials with 30% replacement of the dolomite in the cementitious mixture with finely ground magnesium nitrate or potash (they had to be dried before grinding) had no noticeable effect on the curing rate and the coating thickness but noticeably reduced the amount of ammonia released during the encapsulation process.

It was further observed that such coated prills were no longer sensitive to atmospheric moisture even at high (80-90%) relative humidity, but were permeable to water but were permeable to water to some extent, to the point that all granules lost their urea cores within two days when submerged in an excess of water (ten times by
weight) at room temperature. All coated granules sank in the water used for extracting the urea coated granules. To overcome this permeability problem, one batch of urea coated granules was separated into three lots and treated as follows:

Lot 1. Untreated control.

Lot 2. The coated granules were dropped into heavy diesel oil and allowed to soak for five minutes. The excess diesel oil was decanted and removed from the granules by centrifuging.

Lot 3. The coated granules were tumbled in a plastic bag and treated with approximately 3% concentrated concrete waterproofing agent (GE:PWR-255; HYDROZO 18 or 16 (Sternson Ltd.), MALAN W or MALAN GN (DuPont Company), or similar products) and tumbled until all particles were well-coated with the liquid. Similar products such as a hot paraffin wax coating may also be effective.

When these lots were subjected to solubility in ten times their weight in cold (20°C) water, it was found that all waterproofed samples retained better than 30% of their urea cores for 6 days, and the GE:PWR-255 sample lot retained 30% of its cores for 18 days, and 12% of the cores survived for up to 26 days of soaking (i.e., they at least had one-half of the core within the shell when the
granules were removed from the water and cracked open).

EXAMPLE VI

Twenty grams of polystyrene beads of about 5 mm diameter were treated with 15 mL of ammonium polyphosphate solution in a plastic bag and tumbled to distribute the liquid evenly over the beads. The wet mixture was then treated with 500 g of MgO containing cementitious mixture consisting of 150 g of dead burned magnesite and 350 g of finely ground olivine powder in a plastic bag. After shaking the bag contents for 3 minutes they were allowed to sit for 7 minutes and then separated into unreacted cement and the encapsulated polystyrene beads. The beads were free flowing and the coating thickness was measured as 0.5 mm.

When the same amount of beads was mixed with 30 mL of ammonium polyphosphate and 55 g of dead burned MgO and the mixture poured into a dish after a brief mixing, the mass solidified in 4.5 minutes giving a rather light slab in which the encapsulated particles were bonded only at their contact points.

A similar product could also be made with the dead burned MgO/olivine cementitious powder mixture when the liquid ammonium polyphosphate cement powder ratio was 0.6 or less. It was noted that olivine could be replaced with wet-ground serpentine or dry marble powder without
appreciable change in the reaction rates and hardness of the coating.

**EXAMPLE VII**

Olivine, serpentine and marble chips (3 mm Ø) were heated in a muffle furnace at 1100°C overnight and ground to -200 mesh in a ball mill (the serpentine was wet milled). These calcined products were mixed with various portions of raw magnesite ore also ground to -200 mesh to produce MgO sources for the various coating applications.

Monolithic coatings of 0.2 to 0.6 mm thickness were produced on perlite, polystyrene beads as well as wood particles (sawdust) by the procedures described in Examples I and VI. The coatings had only slight color variations depending on the source of the calcined components of the coatings.

Enhanced fire resistance was observed especially on the encapsulated perlite and wood particles.

**EXAMPLE VIII**

Trials with asbestos fibre encapsulation by the process described in Example I was only partly successful in that it was difficult to keep individual fibers and fiber segments detached from the neighboring fibers. Adhesion of the coatings however were excellent.
To 30 g of fluffy, apparently well separated filter aid grade asbestos mineral fiber was mixed with 20 mL of ammonium polyphosphate liquid in a plastic bag until the liquid was well dispersed and adsorbed by the fibers. After gently tumbling the fibre mass it was allowed to stand for 15 minutes at 21°C.

The fibre material was then added to 250 g of 250 mesh MgO containing cementitious powder mix consisting of 80% dead burned magnesite (Kaiser refractories) and 20% calcined olivine weighted into a plastic bag. The mixture was gently tumbled for 2 minutes whereupon the fibre cement mixture was allowed to cure for 10 minutes. The hardened fibre-cement powder mixture was separated on an 80 mesh sieve. Apart from a few larger fibre lumps which consisted of well bonded asbestos fibres, most of the fibres were well separated. The apparent fibre diameter increased from 100 μm to 500 to 700 μm showing uniform surface coating (encapsulation). The weight increase on the fibres due to the coating (including the lumps) was 38.3 g. The coating appeared to be well adhered to the fibres and the lumps were well bonded.

EXAMPLE IX

A similar attempt with Asplund mechanical fibres as described in Example VIII was much less successful in producing detached encapsulated fibres. Therefore it was decided that spray
coating should be attempted. The fluffed fibre mass showed a very strong tendency to bunch up as soon as the ammonium polyphosphate solution was added and possibly due to the light weight of such fibers they tended to bunch up rather than separate on addition of the cement solids. The fibres consisted mainly of western Canadian species possibly Douglas-fir, western red cedar and true fir.

A large lump of about 2.5 kg of dried Asplund pulp was loaded into the hopper of a two-stage fibre blowing apparatus wherein the fibres were effectively mixed with air in the first stage. The fibre-air mixture was further fed into the second stage fluidizing chamber along with metered amounts of dead burned magnesite laced with metered amounts of dead burned magnesite laced with about 2% MgO heavy powder to increase the reaction speed. The fibre-air-cement mixture was pumped through a 5 m hose which had small nozzles projecting about 20 cm ahead of the hose and spraying well atomized ammonium polyphosphate into the fibre-air-cement mixture. The second air pressure was so adjusted that the exiting fibre-cement mass was allowed to expand (slow) rapidly and be wetted by the liquid. The coated fibres were allowed to fall some distance gently supported by an up-flow of warm air. On the ground a mat of loose fibres were collected which had considerable amounts of ununiformly attached MOP on their surface.
The fibres thus produced were rigid after drying and showed properties of mineralized fibres, and good fire resistance.

EXAMPLE X

In an experiment similar to that of Example VIII mineral wool (KAFCOAT H) and glass fibres prepared from insulation matting (phenol formaldehyde coated) were mixed in a plastic bag with polyphosphoric acid (1:0.5 ratio) until well dispersed. To this wet material a large excess (500 g) of MgO containing 20% calcined magnesite and 80% olivine was added with tumbling until most of the fibres were coated. Again considerable lump formation was noted, however, the lumps were well bonded by MOP while the fibres which remained separated were well coated. The dried fibres were quite stiff and could be handled better like particles than would be expected of fibres which form bundles of irregular form. Some chipping of the coating was noted on the glass fibres when such were tumbled in a bag to simulate mechanical handling.

EXAMPLE XI

To demonstrate the wide utility of the invention for controlled coating of particulate materials, both as to the composition and thickness of the coating, a series of samples was prepared in which control of the adhered coating
thickness was varied by application of limited amounts (down to about 1.5% by weight) of ammonium polyphosphate (10:34:00) to approximately 100% potash granules having a mean diameter of 2.67 mm (range 1.5 mm to 3.8 mm). The excess mineral solids composition was varied from 100% dead burned MgO (Kaiser Refractories Ltd.) to 100% ground KCl (100% passing 100 mesh and 70% passing -200 mesh).

In general, the procedure outlined in Example I was followed, except that in the case of 100% KCl coating the reaction time was 40 minutes in the KCl powder to assure completion of the reaction and some desiccation. The reaction between KCl and the liquid phosphate was indicated by evolution of ammonia gas.

Results of this test series are summarized in Table 1.
### TABLE 1. Variation of coating thickness on potash (KCl).

<table>
<thead>
<tr>
<th>COATING COMPOSITION</th>
<th>ApPh, g/100 g</th>
<th>MINERAL(^1), g/100 g</th>
<th>WEIGHT GAIN, %</th>
<th>COATING THICKNESS, mm</th>
<th>ø</th>
</tr>
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<tbody>
<tr>
<td>100% MgO</td>
<td>1.5</td>
<td>3.91</td>
<td>4.61</td>
<td>0.015</td>
<td>2.70</td>
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<td></td>
<td>2.5</td>
<td>4.53</td>
<td>6.03</td>
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<td>5</td>
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<td>13.80</td>
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<td></td>
<td>10</td>
<td>27.50</td>
<td>32.50</td>
<td>0.175</td>
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<td>12.5</td>
<td>35.67</td>
<td>41.92</td>
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<td>3.11</td>
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<td>2.75</td>
<td>3.5</td>
<td>0.025</td>
<td>2.72</td>
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1Amount of mineral absorbed as coating material on application of prescribed amount of potash.
It is apparent from the table that coating density is highest with the 100% MgO and lowest with KCl. Relatively good coating thickness control can be obtained in this way. It is further found that coatings containing in excess of 70% KCl in their mixture with dead-burned MgO readily disintegrated into a sand-like material when dropped into water. On the other hand, sample coatings made with 50:50 MgO:KCl were insoluble in tap water (pH=6.3), as were those made with 100% MgO. The foregoing exemplary results were achieved when using coating mixtures made up of KCl and dead-burned MgO. The quality of the MgO used was also found to have a significant impact on the solubility of the coatings, so that when using higher quality MgO, lesser percentages were required for the coating to be rendered insoluble. For example, when using heavy powder MgO, it was found that only 3-5% was needed to render the coating insoluble, and 10-20% calcined MgO was necessary to do this, while, as noted above, when using dead-burned MgO, about 30% MgO was required for insolubility. In other words, the higher the quality of the MgO used, the greater the percentage of potash which can be tolerated in the coating mixture before the coating develops a tendency to disintegrate in water.

Such insoluble coatings not only protect the otherwise water-soluble chemicals encapsulated therein, but also slow down the dissolution process itself. Also, on degradation
(dissolution) of the coatings, the coating materials can act as buffers (being made up of magnesium and potassium phosphates), and thus counteract acidification of soils by chlorides and CO₂ and other anions.

Only minor variations in coating thickness (as determined by direct measurement of average particle size before and after coating) are noted on account of changes in the composition of the coating mineral contents. Importantly, coatings can also be made using 100% KCl as the reactive powder. Even such coatings provide considerable protection against moisture and allow the manufacture of coated potash with a minimum amount of change in the K₂O concentration, resulting in positive rather than negative effects on the environment.

EXAMPLE XII

An experiment similar to that described in Example XI was run to demonstrate the feasibility and flexibility of varying the protective mineral coating thickness on urea prills. One series was made up with 100% MgO as the mineral component as applied to commercial grade (AGRICO) urea having an average diameter of 2.55 mm (range from 1.9 mm to 3.05 mm). A second series of samples was made up with a coating mixture consisting of 30% MgO (dead burned) and 70% of a second component consisting of -200 mesh dolomite and -200 mesh KCl powders mixed in a 50:50 ratio. To the KCl 0.005%
of boron was added in the form of borax. The coating thickness was controlled by application of different amounts (between 1.5 to 12.5 g ammonium polyphosphate per 100 g urea granules) of liquid phosphate (10:30:00) or superphosphoric acid. The results are summarized in TABLE 2.
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<th>COATING COMPOSITION</th>
<th>ApPh, g/100 g</th>
<th>MINERAL, g/100 g</th>
<th>WEIGHT GAIN, %</th>
<th>COATING THICKNESS, mm</th>
<th>PARTICLE DIAMETER, mm</th>
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<tr>
<td>30% MgO : 70% (50/50 Dolomite : KCl); trace Borax</td>
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<td>3.79</td>
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</table>

1 Amount of mineral absorbed as coating material on application of prescribed amount of potash.
This process was found to produce uniformly coated urea granules. The higher weight gains on the urea (in comparison to the potash) originate from the lesser porosity and hence lesser absorption of ammonium polyphosphate in the granules. It is also apparent that no ammonium polyphosphate reactivity is lost on the urea surface, whereas a substantial amount (up to 2/3 to 1/2) of the phosphate reacts with the potash and is not available for reaction with MgO in the coating mixture. Thus porous granular particles should be able to carry substantial amounts of ammonium polyphosphate to provide instantly soluble nitrogen (ammonia) on wetting. Thus traditionally monotone fertilizers, such as potash and urea for example, can be upgraded to multi-component fertilizers by this process. Dilution of the main nutrient component becomes possible within wide limits without the need for blending various grades and nutrients as currently in practice.

When the process was repeated on the 10 g/100 g urea sample coated with the 30% MgO : 70% (50/50 Dolomite:KCl) mixture, by reapplication of 10 g of ammonium polyphosphate on 100 g of coated urea, an additional weight gain of 41% (identical to the first application) was obtained. The mean particle diameter increased to 3.33 mm. It is thus demonstrated that the process can be repeated as many times as desired, or until the desired particle diameter is reached.
The coating methods and compositions of the present invention exhibit a number of advantageous aspects, several of which relate specifically to the coating of fertilizer granules. Firstly, the coatings provided by the present invention inhibit the hygroscopic tendencies of common granular fertilizer materials. For example, uncoated hygroscopic fertilizer granules normally have to be stored in sealed plastic bags; otherwise, the granules absorb water, which breaks down the crystalline structure and causes "blooming" of the material at the surface of the granules. If this happens, excessive dust will be generated when applying large quantities of the fertilizer.

Furthermore, the fertilizer granules can become bonded together in a solidified mass, which renders the fertilizer useless unless it is ground up or dissolved. The coatings in accordance with the present invention inhibit these undesirable hygroscopic actions.

A second advantage which relates directly to the use of the present invention to coat fertilizer granules is that the coating is relatively heavy (typically, 1.8-2.5 g/cm³), which increases the density of the coated fertilizer granules; this increased density permits the granules to be broadcast (i.e., thrown) further by mechanical fertilizer spreaders, increasing their coverage. Also, in typical granular fertilizers, 30-50% of the granules are undersized; this can be corrected using the present invention by repeatedly coating and then sieving the granules.
in a continuous process, so as to produce granules of uniform size.

Other significant advantages flow from the relationship between the chemical compositions of the coating and the fertilizer granule itself. For example, as noted above, the coating acts as a buffer which compensates for the acidity which would otherwise build up in the soil as the fertilizer is released. Normally, when urea and potash fertilizers are applied (as to a lawn), this can cause burning unless there is a subsequent application of lime or dolomite. However, the present invention permits the magnesium and/or calcium to be included as part of the coating, and this is released simultaneously with the release of the fertilizer from the granule, therefore eliminating the need for a separate application of lime or dolomite. The coated fertilizer granules thus have the combined effect of separate applications of uncoated fertilizer granules and dolomite or lime.

Apart from the buffering effect described above, the coating of the granules in accordance with the present invention enables the overall chemical make-up of the granules to be adjusted and/or augmented. For example, it is often economically advantageous to produce fertilizer granules having a uniform N-P-K (nitrogen-phosphorous-potassium) ratio, yet it is well known that various species of plants, as well as various types of soils, have specific requirements which may vary from this basic N-P-K ratio. However, by
varying the composition of the coating in the manner which is permitted by the present invention, this N-P-K ratio can be adjusted as desired; for example, when coating potash fertilizer granules, as illustrated in Example XI above, the potash (KCl) and liquid phosphate ratios in the coating can be selected with respect to the N-P-K ratio of the underlying granular potash substrate to adjust the overall N-P-K ratio of the finished fertilizer. In other words, by means of the present invention, one can use the coating to build on a basic granular composition to obtain various N-P-K ratios as desired for specific plant or soil applications.

As was also noted above, the reaction between the principal coating components is relatively insensitive to "impurities". Thus, one can incorporate specific "impurities" in the coating which are beneficial in nature, and which tailor the finished fertilizer to a specific requirement. For example, micronutrient materials can be incorporated into the coating to correct soil deficiencies; small amounts (e.g. 0.001-0.5%) of micronutrients such as iron and boron can be incorporated into the coating mixture so that these are released into the soil with the fertilizer. Similarly, pesticides, herbicides, and like compounds can be incorporated into the coating. Extensive investigation has failed to uncover any commercially significant additives which would inhibit the reaction of the coating materials in the concentrations which normally
would be required, with the exception of boric acid (a source of boron), and it has been found that the inhibiting effect exhibited by this compound can be overcome by heating during the coating reaction. Other "impurities" which can usefully be incorporated into the coating in accordance with the present invention, include ferrous sulphate (e.g., 3%), which is useful in moss control, and lignosulfonic acid (a pulp industry by-product) or elemental sulfur, these being sources of sulphur for sulphur deficient soil.

Since many other modifications and changes varied to fit particular requirements and environments will be apparent to those skilled in the art, the invention is not considered limited to the examples chosen for purposes of disclosure, and covers all changes and modifications which do not constitute departures from the true spirit and scope of this invention.
What Is Claimed Is:

1. A method for encapsulating particulate matter, said method comprising the steps of:
   applying to said particulate matter a liquid phosphate solution so that said liquid phosphate contacts the surfaces of individual particles of said particulate matter;
   applying to said particulate matter a particulate material capable of reacting with said liquid phosphate so as to form a wet phosphate paste which coats said surfaces of said particles; and
   curing said wet phosphate paste until said paste is solidified on said surfaces of said particles so that said particles are encapsulated by said solidified paste.

2. The method of claim 1, wherein the step of applying said particulate material capable of reacting with said liquid phosphate comprises applying to said particulate matter a particulate alkali-metal or alkaline-earth metal compound.

3. The method of claim 2, wherein the step of applying a particulate alkali-metal or alkaline-earth metal compound further comprises the step of selecting said compound from the group consisting of:
   magnesium oxide heavy powder,
   dead burned magnesite,
   calcined magnesite,
   calcined dolomite,
   calcined olivine,
   calcined serpentine,
calcined marble powder,
raw magnesite,
raw dolomite,
raw olivine,
raw serpentine,
raw marble powder, and
potash.

4. The method of claim 3, wherein the step of applying a liquid phosphate solution further comprises the step of selecting said liquid phosphate from the group consisting of: ammonium phosphate, and phosphoric acid.

5. The method of claim 1, wherein the step of applying said liquid phosphate solution to said particulate matter comprises applying said liquid phosphate solution in an amount sufficient to form a liquid phosphate film of selected thickness on said surfaces of said particles so that said reactive particulate material adheres to said surfaces of said particles.

6. The method of claim 5, further comprising the step of transporting said individual particles of said particulate matter which are coated with said paste until said phosphate paste is cured sufficiently to eliminate surface tackiness, so as to prevent said particles from becoming bound together.

7. The method of claim 6, wherein the step of transporting said particles comprises tumbling said particles in a container.
8. The method of claim 6, further comprising the steps of:

separating said coated particles from excess said reactive particulate material;

and

segregating said coated particles so as to select out coated particles having a predetermined size.

9. The method of claim 8, wherein the step of segregating said coated particles comprises sieving said coated particles so as to separate out said coated particles having said predetermined size.

10. The method of claim 8, further comprising the steps of:

retaining said coated particles from which said coated particles of said predetermined size have been segregated; and recoating said retained particles by substantially continuously repeating the steps of:

applying said liquid phosphate solution;

applying said reactive particulate material;

curing said wet phosphate;

transporting said coated particles; and

segregating said coated particles;

so as to produce a uniform output of coated particles having said predetermined size.
11. The method of claim 1, wherein said particulate matter is granular fertilizer, and wherein said method further comprises the step of applying a supplemental agricultural nutrient to said particulate matter so that said supplemental nutrient is incorporated into said phosphate paste coating for subsequent release upon dissolution of said coating.

12. The method of claim 3, wherein said particulate matter is a granular fertilizer having a first predetermined nitrogen-phosphorous-potassium ratio, and said selected alkali-metal or alkaline-earth metal compound comprises potash, and wherein said method further comprises the step of:

applying said particulate potash and said liquid phosphate to said particulate matter in a ratio which is selected so that said phosphate paste coating which is formed on said granulated fertilizer adjusts the nitrogen-phosphorous-potassium ratio of said fertilizer to a second predetermined ratio.

13. The method of claim 12, wherein said reactive particulate material comprises a mixture of potash and magnesium oxide in a predetermined ratio.

14. The method of claim 12, wherein said reactive particulate material is 100% potash.

15. The method of claim 13, wherein said predetermined ratio of said potash and said magnesium oxide in said mixture is selected to
render said solidified phosphate paste coating insoluble in water.

16. The method of claim 13, wherein said predetermined ratio of said potash and said magnesium oxide in said mixture is selected to result in a said solidified phosphate paste coating having a predetermined density.

17. The method of claim 3, wherein the step of applying said liquid phosphate solution further comprises applying said liquid phosphate solution to said particulate matter in a predetermined amount which is selected to form a said phosphate paste coating having a predetermined thickness.
I. CLASSIFICATION OF SUBJECT MATTER
   (if several classification symbols apply, indicate all)

   According to International Patent Classification (IPC) or to both National Classification and IPC

   Int.Cl. 5 C05G3/00; C05C9/00

II. FIELDS SEARCHED

   Minimum Documentation Searched

   Classification System Classification Symbols

   Int.Cl. 5 C05G; C05C; C05D; C05B

   Documentation Searched other than Minimum Documentation
to the Extent that such Documents are Included in the Fields Searched

III. DOCUMENTS CONSIDERED TO BE RELEVANT

   Category* Citation of Document, 11 with indication, where appropriate, of the relevant passages 12 Relevant to Claim No. 13

   X WO, A, 8 704 452 (GATYY TECHNIQUE S.A.) 30 July 1987 1, 2, 4, 5
   A see claims 1, 11, 14
   see example 2

   A GB, A, 894 919 (IMPERIAL CHEMICAL INDUSTRIES LIMITED) 26 April 1962 1, 2, 5-9,
   see claims 1, 3, 9, 10, 12-14

   A CHEMICAL ABSTRACTS, vol. 112, no. 9, 26 February 1990, Columbus, Ohio, US; abstract no. 75873B, 1, 2, 4, 11
   ZHDANOV, YU ET AL.: 'METHOD OF PRODUCING NONCAKING GRANULAR COMPLEX FERTILIZER'
   page 684; see abstract

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   * Special categories of cited documents 10

   "A" document defining the general state of the art which is not considered to be of particular relevance

   "E" earlier document but published on or after the international filing date

   "L" document which may throw doubts on priority claims(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

   "O" document referring to an oral disclosure, use, exhibition or other means

   "P" document published prior to the international filing date but later than the priority date claimed

   "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

   "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

   "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

   "A" document member of the same patent family

IV. CERTIFICATION

   Date of the Actual Completion of the International Search 30 JUNE 1992
   Date of Mailing of this International Search Report 16. 07. 92

   International Searching Authority EUROPEAN PATENT OFFICE
   Signature of Authorized Officer RODRIGUEZ FONTAO M.B
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<td>CHEMICAL ABSTRACTS, vol. 105, no. 15, October 1986, Columbus, Ohio, US; abstract no. 1328930, PLYSHEVSKII, S.V. ET AL.: 'UREA WITH A PHOSPHATE COATING' page 587 ; see abstract</td>
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Form PCT/ISA/210 (extra sheet) (January 1985)
This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on
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