

---

**(12) PATENT ABRIDGMENT      (11) Document No. AU-B-52307/90**  
**(19) AUSTRALIAN PATENT OFFICE      (10) Acceptance No. 628951**

---

(54) Title  
**DETERGENT GRANULES**

International Patent Classification(s)  
(51)<sup>5</sup> **C11D 003/386**

(21) Application No. : **52307/90**

(22) Application Date : **28.03.90**

(30) Priority Data

|                |                 |                          |
|----------------|-----------------|--------------------------|
| (31) Number    | (32) Date       | (33) Country             |
| <b>8907346</b> | <b>31.03.89</b> | <b>GB UNITED KINGDOM</b> |

(43) Publication Date : **04.10.90**

(44) Publication Date of Accepted Application : **24.09.92**

(71) Applicant(s)  
**ECC INTERNATIONAL LIMITED**

(72) Inventor(s)  
**HOWARD GOODMAN**

(74) Attorney or Agent  
**CARTER SMITH & BEADLE , Qantas House, 2 Railway Parade, CAMBERWELL VIC 3124**

(56) Prior Art Documents  
**US 4695511**  
**US 4632768**

(57) Claim

1. A granular chemical reagent for use in a granular detergent composition chosen from an enzyme, a bleaching reagent, a bleach activator, an optical brightening agent, or a mixture of two or more of the aforesaid, the surfaces of the granules of the chemical reagent being provided with a coating comprising an organophilic clay mineral.

11. A process for preparing a coated granular chemical reagent for use in a granular detergent composition selected from an enzyme, a bleaching reagent, a bleach activator, an optical brightening agent, or a mixture of two or more of the aforesaid, which process includes the step of providing the chemical reagent with a coating comprising an organophilic clay mineral.

22. A method for delaying the release into aqueous solution of a granular chemical reagent for use in a granular detergent composition selected from an enzyme, a bleaching reagent, a bleach activator, an optical brightening agent, or mixture of two or more of the aforesaid, which method includes the step of providing the chemical reagent with a coating comprising an organophilic clay material.



The invention relates to improved chemical reagent granules suitable for incorporation in a detergent composition and to a process for preparing the  
5 granules. More particularly, the present invention provides a method for delaying the release into aqueous solution of a chemical reagent used in a detergent composition.

Enzyme granules of the type used in detergent  
10 compositions are sensitive to their surroundings, and their activity tends to decrease with time when mixed with other ingredients to form a detergent composition, even in a relatively dry state. When a detergent composition containing enzyme granules is mixed with  
15 water, dissolution of the enzyme is especially rapid, and when the detergent composition also contains granules of a bleaching reagent, the bleaching reagent is also rapidly released into solution and there is a tendency for the enzyme and the bleaching reagent to  
20 react with one another, rather than to perform their respective desired functions in the washing and cleaning process. It would clearly be desirable to delay the dissolution of the enzyme and/or the bleaching reagent.

25 EP-0051987 discloses a granular bleach activator composition comprising at least 55% by weight of a finely-divided organic peroxy acid bleach precursor, from 1% to 25% by weight of an organic binding agent and from 1% to 25% by weight of a finely-divided water-  
30 insoluble natural or synthetic silica or silicate.

According to a first aspect of the invention, there is provided a granular chemical reagent for use in a granular detergent composition, the surfaces of the granules of the chemical reagent being provided  
35 with a coating comprising an organophilic clay mineral.

The chemical reagent coated may be any one or more

of the chemical reagents employed in detergent compositions such as (a) an enzyme, for example, an amylase, a protease, or a lipase, (b) a bleaching reagent such as sodium perborate or  
5 diperoxydodecandioic acid, or (c) a bleach activator such as methyl o-acetoxy benzoate, sodium p-acetoxy benzene sulphonate, bisphenol A diacetate, tetra acetyl ethylene diamine, tetra acetyl hexamethylene diamine or tetra acetyl methylene diamine, or (d) an optical  
10 brightening agent.

According to a second aspect of the invention, there is provided a process for preparing a granular chemical reagent for use in a detergent composition, which process includes the step of providing the  
15 chemical reagent with a coating comprising an organophilic clay mineral.

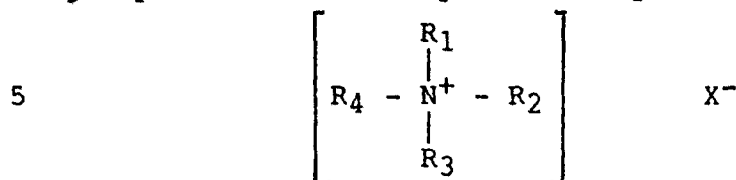
According to a third aspect of the present invention, there is provided a method for delaying the release of a chemical reagent used in a detergent  
20 composition, which method includes the step of providing the chemical reagent with a coating comprising an organophilic clay mineral.

The clay mineral may, for example, be a smectite clay, for example bentonite, montmorillonite,  
25 hectorite, saponite, fullers earth or the like. A bentonite of which the major part of the exchangeable cations are sodium ions (a sodium bentonite) is especially suitable. Other bentonites such as calcium bentonite are also suitable. Alternatively, the clay  
30 mineral may be a kaolin clay.

The clay mineral may be rendered organophilic by treatment with a quaternary ammonium compound having at least one higher alkyl group containing from 10 to 24 carbon atoms. This is particularly suitable for  
35 rendering a smectite clay mineral organophilic.

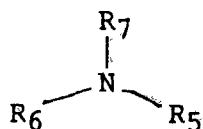
The quaternary ammonium compound preferably

consists of one or more components chosen from the group which can be represented by the general formula:



in which  $R_1$  is a saturated or unsaturated alkyl group having from 10 to 24 carbon atoms,  $R_2$  and  $R_3$ , which may  
 10 be the same or different, are each a saturated or unsaturated alkyl group having from 1 to 24 carbon atoms or an aralkyl group having from 7 to 10 carbon atoms,  $R_4$  is an alkyl group having from 1 to 6 carbon atoms or an aralkyl group having from 7 to 10 carbon  
 15 atoms and  $X$  is  $OH$ ,  $Cl$ ,  $Br$ ,  $I$ ,  $NO_2$ ,  $CH_3SO_4$  or  $CH_3.COO$ . Examples of such quaternary ammonium compounds are the methyl benzyl dialkyl ammonium chlorides, the dimethyl dialkyl ammonium chlorides, the dimethyl benzyl alkyl ammonium chlorides, the benzyl trialkyl ammonium  
 20 chlorides and the methyl trialkyl ammonium chlorides. The alkyl group is most advantageously a mixture of hydrocarbon radicals derived from tallow having from 14 to 20 carbon atoms but in which  $C_{18}$  radicals predominate. (A typical analysis of such a mixture of  
 25 hydrocarbon radicals contained in tallow is:  $C_{14}$  4.5%;  $C_{15}$  0.5%;  $C_{16}$  30.5%,  $C_{17}$  1.5%;  $C_{18}$  62.0% and  $C_{20}$  1.0%). The hydrocarbon radicals may be substantially saturated as a result of, for example, treating the tallow with  
 hydrogen in the presence of a suitable catalyst.

30 The clay mineral may alternatively be rendered organophilic by treatment with an organic amine, preferably one having at least one higher alkyl group containing from 10 to 24 carbon atoms. The organic amine may be a primary, secondary or tertiary amine of  
 35 general formula



in which  $R_5$  is a saturated or unsaturated alkyl group having from 10 to 24 carbon atoms, and  $R_6$  and  $R_7$ , which may be the same or different, are each a hydrogen atom or a saturated or unsaturated alkyl group having from 1  
5 to 24 carbon atoms or an aralkyl group having from 7 to 10 carbon atoms. One presently preferred amine is octadecylamine.

The clay mineral is treated with sufficient of the quaternary ammonium compound or organic amine to render  
10 it organophilic. Preferably the clay mineral is treated with sufficient of the quaternary ammonium compound or amine to provide up to 155, and preferably no more than 140, milliequivalents (meq.) of quaternary ammonium compound or amine per 100g of dry clay. Where  
15 the organophilic clay mineral is prepared by a "wet" process, for example one in which a suspension of the clay mineral is mixed with a dispersion of quaternary ammonium compound, the resultant organophilic clay mineral will normally have at least 90 milliequivalents .  
20 of the quaternary ammonium compound per 100g of dry clay. It is possible to prepare an organophilic clay mineral containing very much less than 90 meq. of the quaternary ammonium compound or amine by a process of dry mixing the clay mineral with a molten amine or  
25 molten quaternary ammonium compound. Further improvements have been achieved when the clay mineral is combined with the quaternary ammonium compound under conditions of strong mixing in order to produce a well dispersed organophilic clay mineral.

30 The clay mineral ~~should~~ preferably have a particle size such that at least 90% of the particles pass through a No. 200 mesh British Standard sieve (nominal aperture 76 microns).

The chemical reagent granules may be coated with  
35 the organophilic clay mineral by, for example, tumbling the granules in a pan granulator while spraying them



with a suspension of the organophilic clay mineral in a suitable liquid medium such as a liquid aliphatic hydrocarbon. Alternatively the chemical reagent granules may be mixed with the organophilic clay mineral in substantially dry powder form in, for example, a pan granulator and the mixture sprayed with a liquid binder such as a liquid aliphatic hydrocarbon or an aqueous suspension of an organic polymeric binder which may be, for example, a natural or synthetic polyisoprene, a styrene-butadiene copolymer, a lower alkyl acrylic acid ester - lower alkyl methacrylic acid ester copolymer, a copolymer of a lower alkyl acrylic acid ester and/or a lower alkyl methacrylic acid ester with vinyl acetate, styrene or acrylonitrile, a poly(vinyl acetate), a poly(vinyl alcohol) or a copolymer of vinyl acetate with styrene and/or acrylonitrile.

Preferably the chemical reagent granules are coated with from 0.1 to 20% by weight, based on the weight of dry chemical reagent granules, of the organophilic clay mineral. More preferably, the granules are coated with no more than 10% by weight of the organophilic clay mineral.

Where an organic polymeric binder is used, the amount of this binder is preferably from 1% to 20% by weight, based on the weight of dry chemical reagent granules.

Even more advantageous results are obtained when there is mixed with the organic polymeric binder up to about 15% by weight, based on the weight of dry chemical reagent granules, of a finely divided mineral material. The mineral material may be, for example, a kandite clay mineral, i.e. kaolinite, nacrite, dickite or halloysite, a smectite clay mineral, calcium carbonate, talc, mica or gypsum. Generally not more than about 10% by weight, based on the weight of dry

chemical reagent granules, of the finely divided mineral material will be required. It is believed that the particles of the finely divided mineral material serve to seal gaps left on the surface of the chemical reagent granules between the particles of the organophilic clay mineral.

The coated chemical reagent granules of the present invention may be used with advantage in granular detergent compositions, such as conventional washing powders. In such circumstances, the coated reagent of the present invention replaces the uncoated reagent conventionally used.

A typical detergent composition may contain one or more of the following ingredients within the following ranges:-

|    | <u>Ingredient</u>                | <u>% by weight</u> |
|----|----------------------------------|--------------------|
|    | Anionic surfactant               | 0-25               |
|    | Nonionic surfactant              | 2-35               |
|    | Suds controlling agent           | 0-5                |
| 20 | Foaming booster                  | 0-2                |
|    | Enzyme granules                  | 0.1-2.3            |
|    | Builder                          | 0-25               |
|    | Formulation aid                  | 3-15               |
|    | Optical brightener               | 0.1-0.3            |
| 25 | Stabiliser                       | 0-5                |
|    | Fabric softener                  | 0-2                |
|    | Fragrance, dyestuff and water to | 100                |

The anionic surfactant may be chosen from the group consisting of alkylbenzene sulphonates, soaps and fatty alcohol ether sulphates. The nonionic surfactant may be, for example, an alkyl polyethyleneglycol ether. The suds controlling agent may be, for example, a soap. The foaming booster may be, for example, a fatty acid alkanol amide. The builder may be chosen from the group consisting of potassium diphosphate, sodium triphosphate, sodium citrate and sodium silicate. The formulation aid may be chosen from the group consisting of xylene sulphonates, ethanol and propylene glycol. The optical brightener may be, for example, a stilbene-disulphonic acid-bis-(styryl)-biphenyl derivative.

The stabiliser may be triethanolamine or another complexing agent. The fabric softener may be a smectite clay or a quaternary ammonium compound.

The invention will now be illustrated by the following examples.

#### EXAMPLE 1

In this example 100g of enzyme granules comprising an amylase concentrate and a suitable binder and having diameters substantially within the range from 0.5 to 1.0 mm were tumbled in a pan granulator and were mixed with

- either A: 10g of a natural hydrophilic calcium bentonite having a particle size distribution such that 99% by weight passed through a No. 300 mesh British Standard sieve (nominal aperture 53 microns).
- or B: 7g of a Wyoming sodium bentonite which had been treated with sufficient dimethyl di(hydrogenated tallow) ammonium chloride (2M2HT) to provide 135 milliequivalents of 2M2HT per 100g of dry bentonite and having a particle size distribution such that 99% by weight passed through a No. 200 mesh British Standard sieve (nominal aperture 76 microns).

The substantially dry mixture of enzyme granules and either A or B was sprayed with a known weight of

- (a) water
- or (b) a styrene-butadiene rubber latex containing 50% by weight of latex solids (SBR latex)
- or (c) odourless mineral spirit - a substantially aliphatic liquid hydrocarbon (OMS)

The coated granules were then dried in a vacuum oven at 60°C. In a cylindrical vessel which had a base portion which was separated from the body of the vessel by a millipore filtration membrane having a pore size of 0.45 microns there was then placed 300ml of distilled water. The base portion was provided with an outlet for filtrate passing through the membrane, the outlet being closable with a valve. The vessel was also provided with a close fitting lid provided with an inlet for connection to a supply of air at superatmospheric pressure. Suspended from the lid by means of a shaft was a magnetically rotated stirrer and a cup for containing a sample of dried coated granules; 1.5g of each batch of coated granules was placed in turn in the cup and the vessel was sealed and placed under pressure. The valve at the base portion of the vessel was then opened for a time sufficient to draw off 7-8 ml of dead liquid which had passed through the membrane. With the magnetic stirrer rotating, the vessel was shaken to transfer the granules from the cup into the water and a stop watch was started. At given intervals there was run off from the base portion of the vessel firstly 7-8 ml of dead liquid, then 7-8 ml of a sample which was tested for percentage absorption of ultraviolet light of wavelength 269 nm in an ultraviolet spectrophotometer. The particular amylase enzyme used was found to absorb strongly at a wavelength of 269 nm and the percentage absorption of radiation of this wavelength therefore gave a measure of the concentration of amylase in solution. A graph was drawn of percentage absorption against time and a value was obtained for "t<sub>50</sub>", the time at which the percentage absorption was 50% of the maximum percentage absorption obtainable.

As a comparison a value of t<sub>50</sub> was also obtained for the uncoated enzyme granules.

The results obtained are set forth in table I below:-

Table I

|    | Coating      | Binder    | Percentage by weight of binder on granules | t <sub>50</sub> (mins.) |
|----|--------------|-----------|--------------------------------------------|-------------------------|
| 5  | Clay mineral |           |                                            |                         |
|    | None         | -         | -                                          | 0.20                    |
|    | A            | Water     | -                                          | 0.20                    |
|    | A            | SBR latex | 2.6                                        | 0.35                    |
| 10 | A            | SBR latex | 13.4                                       | 0.65                    |
|    | None         | SBR latex | 16.8                                       | 2.0                     |
|    | B            | OMS       | 11.0                                       | 1.0                     |
|    | B            | SBR latex | 10.0                                       | 0.9                     |

These results show that with an organophilic clay mineral B in accordance with the invention less binder is required to produce a significant reduction in the rate of dissolution of the enzyme granules as compared with a coating of a hydrophilic clay mineral A.

EXAMPLE 2

20 A suspension of an organophilic clay mineral in odourless mineral spirit (OMS) was prepared by first adding 7.2 ml of propylene carbonate, as a polar activator, to 315g of OMS in a 1 litre paint tin. There was then poured slowly into this mixture, which 25 was continuously stirred by means of a small Cowles blade rotating on a laboratory stirrer at 4000 rpm, 31.5g of an organophilic clay mineral which had been prepared by treating a Wyoming sodium bentonite with sufficient 2M2HT to provide 95 milliequivalents of 30 2M2HT per 100g of dry bentonite and which had a particle size distribution such that 95% by weight passed through a No. 200 mesh British Standard sieve. Mixing was continued for 15 minutes after the addition of the clay mineral was complete.

35 Next, 100g of the same enzyme granules as were used in Example 1 were tumbled in the pan granulator

and known weights of the organophilic clay mineral suspension were sprayed on to the granules until the granules were well moistened and started to stick together. The coated granules were then dried in the vacuum oven at 60°C. The coating procedure was then repeated until a sufficient layer of the organophilic clay mineral had been built up.

Samples of the coated granules were then tested as described in Example 1 above to determine the  $t_{50}$  for the enzyme. The results obtained are set forth in Table II below:-

Table II

|    | Percentage by<br>weight of organophilic<br>clay mineral on<br>granules | $t_{50}$ |
|----|------------------------------------------------------------------------|----------|
| 15 | 0.24                                                                   | 0.30     |
|    | 0.93                                                                   | 0.80     |
|    | 1.80                                                                   | 2.5      |

20 These results show that comparable reductions in the rate of dissolution of the enzyme to those obtained in Example 1 are obtainable with very much smaller amounts of the organophilic clay mineral if the organophilic clay mineral is well dispersed.

25 EXAMPLE 3

In this example, 100g batches of enzyme granules, which were similar to those used in Example 1 except that the amylase concentrate was of higher activity and different binder and pelletiser were used so that the rate of dissolution of enzyme from the uncoated granules was less rapid, were mixed in the pan granulator with 7g of the same organophilic clay mineral as was used in Example 1B using OMS or different amounts of SBR latex as the binder. In each case the value of  $t_{50}$  for the rate of dissolution of the enzyme was determined as described in Example 1.

As a comparison the value of  $t_{50}$  for the uncoated enzyme granules was also determined.

The results are set forth in Table III below:-

Table III

| 5  | Binder    | Percentage by                   | $t_{50}$ |
|----|-----------|---------------------------------|----------|
|    |           | weight of binder<br>on granules |          |
|    | OMS       | 11.0                            | 4.0      |
|    | SBR latex | 1.8                             | 2.8      |
| 10 | SBR latex | 5.8                             | 4.0      |
|    | SBR latex | 9.4                             | 3.0      |
|    | None      | -                               | 1.5      |

**EXAMPLE 4**

In this Example, 100g of the same enzyme granules as were used in Example 3 were rotated in the pan granulator and were sprayed with a suspension in

5 ordcurless mineral spirit of the same organophilic clay mineral as was used in Example 1. The suspension was prepared by first adding 7.2 ml of propylene carbonate to 315g. of OMS in a 1 litre paint tin. Next, 31.5g of

10 the organophilic clay mineral was poured slowly into this mixture, which was continuously stirred by means of a small Cowles blade rotating on a laboratory stirrer at 4000 rpm. The mixing was continued for 15 minutes after the addition of the clay mineral was complete. A known weight of the suspension was sprayed

15 on to the granules until the granules were well moistened and started to stick together. The coated granules were then dried in the vacuum oven at 80°C. The procedure of coating and drying was then repeated until a sufficiently thick layer of the organophilic

20 clay mineral had been built up.

A sample of the coated granules was then tested to determine the  $t_{50}$  for the enzyme as described in Example 1. It was found that a layer containing 1.9% by weight of the organophilic clay mineral, based on

25 the weight of dry enzyme granules, increased the  $t_{50}$  to

6.5 mins. as compared with 1.5 mins. for the untreated granules.

#### EXAMPLE 5

2 kg batches of the same enzyme granules as were used in Example 3 were placed in an Eirich mixer which is a pan granulator which is provided with a high speed rotating agitator and with paddle blades which are rotated at a slower speed and in a direction opposite to the direction of rotation of the pan. There was mixed with the granules either 4% by weight or 7% by weight, based on the weight of dry granules, of the same organophilic clay mineral as was used in Example 1, in dry powder form. The dry mixture was then sprayed either with a known weight of OMS or with a known weight of the same SBR latex as was described in Example 1. The coated granules were then dried in the vacuum oven at 60°C and samples of the coated granules were tested to determine the  $t_{50}$  for the enzyme as described in Example 1.

The results are set forth in Table IV below:

Table IV

| Percentage by wt. of organophilic clay mineral | Binder    | Percentage by weight of binder on granules | $t_{50}$ (mins.) |
|------------------------------------------------|-----------|--------------------------------------------|------------------|
| 4                                              | OMS       | 5                                          | 5.5              |
| 7                                              | OMS       | 9                                          | 6.6              |
| 4                                              | SBR latex | 3                                          | 5.0              |
| 7                                              | SBR latex | 6                                          | 9.0              |

#### EXAMPLE 6

A binder suspension for use in preparing coated enzyme granules in accordance with the invention was formulated by first weighing out 200g of a kaolinitic clay which was in a substantially dry, powdered form, and which had an ultimate particle size distribution such that 80% by weight consisted of particles having an equivalent spherical diameter smaller than  $2\mu\text{m}$  and

0.5% by weight consisted of particles having an equivalent spherical diameter larger than  $10\mu\text{m}$ . 1000g of a styrene-butadiene latex which contained 50% by weight of dry polymer was weighed into a beaker and there were added thereto  $6.0\text{ cm}^3$  of a 10% w/v solution of a sodium polyacrylate dispersing agent (0.3% by weight of sodium polyacrylate based on the weight of dry kaolinitic clay), and  $2.0\text{ cm}^3$  of a 10% w/v solution of sodium hydroxide. The mixture was stirred by means of a Cowles blade rotating on a laboratory stirrer, while the kaolinitic clay powder was slowly added thereto. When all the clay had been added, the resultant mixture was stirred for a further 15 minutes at a stirrer speed of 1500 rpm. in order to ensure thorough mixing. The pH of the suspension was measured and found to be 6.1, and sufficient of the 10% w/v solution of sodium hydroxide was added to raise the pH to 7.0. The mixture was then stirred for a further 5 minutes to complete the preparation of the binder suspension.

1500g of enzyme granules comprising a protease concentrate and a suitable binder, and having diameters substantially within the range from 0.5 to 1.0mm were tumbled with 150g of the organophilic clay mineral described under B in Example 1 in the Eirich mixer, with the pan rotating at a relatively high speed and the agitator rotating at a relatively low speed. The binder suspension prepared as described above was sprayed on to the mixture in the pan of the Eirich mixer from a pressurised water sprayer to produce the finest possible spray. The Eirich mixer was stopped at regular intervals so that the moistened mixture could be scraped from the walls of the pan by means of a spatula. The quantity of the binder suspension found to be necessary was 640g. The coated granules were then removed from the pan and dried in a vacuum oven at

60°C. The enzyme granules were now coated with 10% by weight of organophilic clay, 17.8% by weight of latex solids and 7.1% by weight of kaolinitic clay, all three percentages by weight being based on the weight of dry enzyme granules.

Samples of the coated granules were tested as described in Example 1 above to determine the rate of dissolution of the enzyme and a graph was drawn of percentage absorption of radiation of wavelength 269nm against time. However, instead of the value of "t<sub>50</sub>" being determined, there was read from the graph the percentage absorption at 269nm after a time of 10 minutes.

The experiment was then repeated except that there was used as the binder suspension 280g of the 50% by weight styrene-butadiene latex so that the enzyme granules were coated with 10% by weight of organophilic clay and 8.5% by weight of latex solids, both percentages by weight being based on the weight of dry enzyme granules.

As a further control the percentage absorption at 269 nm after a time of 10 minutes was measured for the uncoated enzyme granules.

The results are set forth in the Table below:-

| Granules                                                   | Absorption at 269nm<br>after 10 minutes |
|------------------------------------------------------------|-----------------------------------------|
| Uncoated                                                   | 0.50                                    |
| Coated with organophilic clay<br>+ latex                   | 0.26                                    |
| Coated with organophilic clay<br>+ latex + kaolinitic clay | 0.10                                    |

From these results it can be seen that the rate of dissolution of the enzyme is greatly reduced by including kaolinitic clay in the binder suspension.

#### EXAMPLE 7

100g. of enzyme granules comprising a protease concentrate and a suitable binder, and having diameters

substantially within the range from 0.5 to 1.0mm, where  
tumbled in a pan granulator and were mixed with 10g of  
a kaolin clay having a particle size distribution such  
that 8% by weight consisted of particles having an  
5 equivalent spherical diameter larger than 10 $\mu$ m. and 50%  
by weight consisted of particles having an equivalent  
spherical diameter smaller than 2 $\mu$ m. and which had been  
treated with 1% by weight based on the weight of dry  
kaolin clay, of octadecylamine, which amount was  
10 sufficient to provide 4 milliequivalents of  
octadecylamine per 100g. of dry clay.

The substantially dry mixture of enzyme granules  
and octadecylamine coated clay in the pan granulator  
was sprayed with 17g of a styrene-butadiene rubber  
15 latex which contained 50% by weight of latex solids.  
The enzyme/organophilic clay granules therefore  
contained 8.5% by weight of latex solids, based on the  
weight of dry enzyme granules.

The coated granules were dried in a vacuum oven at .  
20 60°C and were then tested for the rate of dissolution  
of the enzyme by the procedure described in Example 1.  
The value for "t<sub>50</sub>" for the organophilic clay coated  
enzyme granules was found to be 8.5 minutes.

The claims form part of the disclosure of this specification.

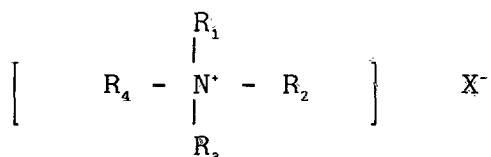
THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. A granular chemical reagent for use in a granular detergent composition chosen from an enzyme, a bleaching reagent, a bleach activator, an optical brightening agent, or a mixture of two or more of the aforesaid, the surfaces of the granules of the chemical reagent being provided with a coating comprising an organophilic clay mineral.

2. A granular chemical reagent according to claim 1, wherein the organophilic clay mineral is an organophilic smectite clay or an organophilic kaolin clay.

3. A granular chemical reagent according to claim 1 or 2, wherein the organophilic clay mineral is prepared by treating a clay mineral with a quaternary ammonium compound having at least one higher alkyl group containing from 10 to 24 carbon atoms.

4. A granular chemical reagent according to claim 3, wherein the quaternary ammonium compound consists of one or more components chosen from the group which can be represented by the general formula:



in which  $R_1$  is a saturated or unsaturated alkyl group having from 10 to 24 carbon atoms,  $R_2$  and  $R_3$ , which may be the same or different, are each a saturated or unsaturated alkyl group having from 1 to 24 carbon atoms or an aralkyl group having from 7 to 10 carbon atoms,  $R_4$  is an alkyl group having from 1 to 6 carbon atoms or an aralkyl group having from 7 to 10 carbon atoms and X is OH, Cl, Br, I,  $NO_2$ ,  $CH_3SO_4$  or  $CH_3COO$ .

5. A granular chemical reagent according to claim 1 or 2, wherein the organophilic clay mineral is prepared by treating a clay mineral with an organic amine having at least one higher alkyl group containing from 10 to 24 carbon atoms.

6. A granular chemical reagent according to claim 3, 4 or 5, wherein the clay mineral is treated with sufficient



of the quaternary ammonium compound or amine to provide no more than 155 milliequivalents of quaternary ammonium compound or amine per 100g of dry clay.

5 7. A granular chemical reagent according to any preceding claim, wherein the chemical reagent granules are coated with from 0.1 to 20% by weight, based on the weight of the dry chemical reagent, of the organophilic clay mineral.

10 8. A granular chemical reagent according to any preceding claim, wherein the chemical reagent is an enzyme, a bleaching reagent, a bleach activator, an optical brightening agent, or a mixture of two or more of the aforesaid.

15 9. A granular chemical reagent according to claim 8, wherein the chemical reagent is an enzyme.

10. A granular detergent composition comprising a granular chemical reagent in accordance with any one of the preceding claims.

20 11. A process for preparing a coated granular chemical reagent for use in a granular detergent composition selected from an enzyme, a bleaching reagent, a bleach activator, an optical brightening agent, or a mixture of two or more of the aforesaid, which process includes the step of providing the chemical reagent with a coating comprising an organophilic clay mineral.

25 12. A process according to claim 11, wherein the organophilic clay mineral is an organophilic smectite clay or an organophilic kaolin clay.

30 13. A process according to claim 11 or 12, wherein the organophilic clay mineral is prepared by treating a clay mineral with a quaternary ammonium compound having at least one higher alkyl group containing from 10 to 24 carbon atoms.

35 14. A process according to claim 11 or 12, wherein the organophilic clay mineral is prepared by treating a clay mineral with an organic amine having at least one higher alkyl group containing from 10 to 24 carbon atoms.

15. A process according to claim 13 or 14, wherein the clay mineral is treated with sufficient of the quaternary ammonium compound or amine to provide no more than 155 milliequivalents of quaternary ammonium compound per 100g of dry clay.

16. A process according to any one of claims 11 to 15, wherein the chemical reagent granules are coated with from 0.1 to 20% by weight, based on the weight of dry chemical reagent, of the organophilic clay mineral.

17. A process according to any one of claims 11 to 16, wherein the chemical reagent granules are coated with the organophilic clay mineral in the presence of a binder.

18. A process according to any one of claims 11 to 17, wherein the chemical reagent granules are coated with the organophilic clay mineral by tumbling the granules in a pan granulator while applying a suspension of the organophilic clay mineral in a liquid binder medium.

19. A process according to any one of claims 11 to 17, wherein the chemical reagent granules are coated with the organophilic clay mineral in dry powder form by tumbling the granules together with the organophilic clay mineral in a pan granulator whilst applying a liquid binder.

20. A process according to claim 17, 18 or 19, wherein the binder is an organic polymer.

21. A process according to claim 20, wherein the organic polymeric binder contains up to about 15% by weight, based on the weight of the dry chemical reagent granules, of a finely divided mineral material.

22. A method for delaying the release into aqueous solution of a granular chemical reagent for use in a granular detergent composition selected from an enzyme, a bleaching reagent, a bleach activator, an optical brightening agent, or mixture of two or more of the aforesaid, which method includes the step of providing the chemical reagent with a coating comprising an organophilic clay material.

23. A granular chemical reagent substantially as hereinbefore described with reference to the Examples.

24. A process for preparing a granular chemical reagent selected from an enzyme, a bleaching reagent, a bleach activator, an optical brightening agent or mixture of two or more of the aforesaid, substantially as hereinbefore described with reference to the Examples.

25. A method for delaying the release into aqueous solution of a granular chemical reagent selected from an enzyme, a bleaching reagent, a bleach activator, an optical brightening agent or mixture of two or more of the aforesaid, substantially as hereinbefore described with reference to the Examples.

DATED this July 25, 1992

**CARTER SMITH & BEADLE**

Fellows Institute of Patent Attorneys of Australia

Patent Attorneys for the Applicant:

**ECC INTERNATIONAL LIMITED**