PCT WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 :		(11) International Publication Number:
B01J 2/00, A01N 25/26, C05G 3/00, A61K 9/28	**A1**	**WO 99/36168**
		(43) International Publication Date: 22 July 1999 (22.07.99)

(21) International Application Number: PCT/GR99/00003

(22) International Filing Date: 11 January 1999 (11.01.99)

(30) Priority Data:
980100026 15 January 1998 (15.01.98) GR

(71)(72) Applicant and Inventor: VALKANAS, George, N. [GR/GR]; 14 Constantinoupoleos Street, GR–151 32 Maroussi (GR).

(74) Agent: KILIMIRIS, Tassos, Anastase; 7 Hatziyianni Mexi Street, GR–115 28 Athens (GR).

(81) Designated States: CN, PL, RU, UA, US, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

Published
With international search report.

(54) Title: METHOD OF PRODUCTION OF ENCAPSULATING MATERIALS OF A BIOLOGICALLY CONTROLLED YIELD

(57) Abstract

A method of production and application of encapsulating materials for medicines, pesticides, fertilisers, pesticides, insecticides, fungicides, is described, which are defined by a system of resins, linear and non–linear paraffin, stearines, polyethylene and polyethylene oxide resins, asphalts, all having a melting point between 80 and 130 degrees Celsius, with a 3–10 % content of polymerised special colophon of the Pinus Halepensis variety with a melting point of 120–130 degrees Celsius which provides cohesion and resin character to the mixture, where the encapsulating materials with a 25–30 % composition are heated to 170 degrees Celsius and where the materials are added to the molten phase in a series according to their stability with a gradual lowering of the temperature to 110–120 degrees Celsius; then the encapsulating material flows and is driven to a pelletiser which converts it to granules or is driven to a crusher system which grinds it and the encapsulated materials are selected so that edible stearines and linear paraffins are used with medicines, a mixture depending on the required yield time is used and a mixture is used with the pesticides, insecticides fungicides that leads to adsorption and absorption from the recipient so that they all contribute to protection of the environment and safety for the food chain.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	**ES**	Spain	**LS**	Lesotho	**SI**	Slovenia
AM	Armenia	**FI**	Finland	**LT**	Lithuania	**SK**	Slovakia
AT	Austria	**FR**	France	**LU**	Luxembourg	**SN**	Senegal
AU	Australia	**GA**	Gabon	**LV**	Latvia	**SZ**	Swaziland
AZ	Azerbaijan	**GB**	United Kingdom	**MC**	Monaco	**TD**	Chad
BA	Bosnia and Herzegovina	**GE**	Georgia	**MD**	Republic of Moldova	**TG**	Togo
BB	Barbados	**GH**	Ghana	**MG**	Madagascar	**TJ**	Tajikistan
BE	Belgium	**GN**	Guinea	**MK**	The former Yugoslav Republic of Macedonia	**TM**	Turkmenistan
BF	Burkina Faso	**GR**	Greece			**TR**	Turkey
BG	Bulgaria	**HU**	Hungary	**ML**	Mali	**TT**	Trinidad and Tobago
BJ	Benin	**IE**	Ireland	**MN**	Mongolia	**UA**	Ukraine
BR	Brazil	**IL**	Israel	**MR**	Mauritania	**UG**	Uganda
BY	Belarus	**IS**	Iceland	**MW**	Malawi	**US**	United States of America
CA	Canada	**IT**	Italy	**MX**	Mexico	**UZ**	Uzbekistan
CF	Central African Republic	**JP**	Japan	**NE**	Niger	**VN**	Viet Nam
CG	Congo	**KE**	Kenya	**NL**	Netherlands	**YU**	Yugoslavia
CH	Switzerland	**KG**	Kyrgyzstan	**NO**	Norway	**ZW**	Zimbabwe
CI	Côte d'Ivoire	**KP**	Democratic People's Republic of Korea	**NZ**	New Zealand		
CM	Cameroon			**PL**	Poland		
CN	China	**KR**	Republic of Korea	**PT**	Portugal		
CU	Cuba	**KZ**	Kazakstan	**RO**	Romania		
CZ	Czech Republic	**LC**	Saint Lucia	**RU**	Russian Federation		
DE	Germany	**LI**	Liechtenstein	**SD**	Sudan		
DK	Denmark	**LK**	Sri Lanka	**SE**	Sweden		
EE	Estonia	**LR**	Liberia	**SG**	Singapore		

METHOD OF PRODUCTION OF ENCAPSULATING MATERIALS OF A BIOLOGICALLY CONTROLLED YIELD

This invention refers to the synthesis and production of encapsulating systems for consumer goods such as medicines, pesticides, fertilisers, insecticides and in general materials, the use of which requires some consumption control so that a slow, controlled yield and complete consumption is achieved. The protection of the environment and mainly the protection of health from the introduction of toxicity via medicines and the protection of the food chain from the concentration of toxic and poisoning substances, requires an efficient handling.

Pesticides, insecticides, weed killers, fungicides, and similar substances are known to be sprayed in quantities several times higher than that required for protection against insects, and weeds; it is also known that only 20 to 40% consumption of fertilisers in the soil is achieved, the remaining quantity constituting a source of environmental pollution; medicines are also taken in quantities far higher than those required and are rapidly metabolised or rejected by the organism.

It is known that the above mentioned products that are widely used, must be introduced in particular methods that will promote a slow controlled quantitative metabolism and for this reason it is necessary to develop encapsulating systems that will lead to a biologically controlled, complete exploitation of the products in order to avoid the creation of toxic conditions in the environment and in every day life. It is also known that any solution provided to this crucial problem, any solution concerning encapsulating of fertilisers

and pesticides exploited in the soil, must be adapted to the needs of the soil which is the principle biological laboratory of the planet. Bearing in mind this concern, encapsulating fertilisers and pesticides must be compatible with the biological activity and the needs of the soil. Thus, encapsulating weed killers, insecticides and fungicides provided by spraying, must lead to an efficiency with the minimum quantity required, so that no concentration of toxic and poisoning materials develops. Furthermore, encapsulating medicines for provision to humans and animals must lead to a degree of efficiency, i.e. to a complete exploitation of the medicine over longer periods of time achieving an economy of expensive medicines and avoiding side-effects.

The composition of encapsulating systems that provide total or partial insolubility in water and that promotes slow yield of the encapsulated substances has been the topic of intensive research and development, so that at present all possible combinations have been studied and patented. These published solutions operate on the principle of mechanical opening and release with partial solubility in water, so that the conditions of slow yield are satisfied. However, these solutions do not constitute a satisfactory answer to the problem, as they do not correspond to the biological functioning and the needs of the recipient.

The inventor has researched, developed and proved in practice an encapsulating system defined by organic resins with a determined biodegradability corresponding to the biological functioning of the recipient controlled by the presence of special polymerised colophon of the variety of pinus halepensis, that provides to the encapsulating system cohesion of the resin character and constitutes the key of biological operation for opening the encapsulating system. The encapsulating system is formed by mixing different resins of

controlled biodegradability, such as linear paraffin, or non-linear paraffin, polyethylene resins, polyethylene oxide resins, stearines, asphalt and others, or mixtures thereof, depending on the use and on the recipient selected so that they have a melting point between 80 and 130 degrees Celsius. To this mixture, the polymerised special colophon of pinus halepensis with a melting point of 120 to 130 degrees Celsius in a3 - 10% composition.

The encapsulating system is defined by the use it is offered for, and the tolerance of the recipient in the toxicity and biological behaviour.

In the case of medicines for internal use for humans and animals, the encapsulating system must not introduce toxicity and is thus selected to be a mixture of edible resins such as stearines and linear paraffins. These components in the presence of special colophon, at a ratio of 2-3%, promote the biological controlled yield of the medicines with sufficient activity and duration of activity with a significant reduction of the quantity of the medicine used.

The encapsulating system for pesticides, insecticides, and fungicides supplied by spraying, must be adsorbed by or absorbed by the recipient for controlling the quantity and efficiency. For these reasons a mixture of polyethylene resins and of polyethylene oxide are selected. With this solution, these sprayed toxic and poisoning materials are totally assimilated with a significant reduction of their consumption, thus avoiding concentration on foodstuffs and fruit and discharge to the environment.

The encapsulating system for fertilisers and soil pesticides is selected so as to correspond to the biological activity of the soil and to have a time of release of the encapsulated species, ranging

between very short periods and very long periods. All the above mentioned resin mixtures are suitable for this use. The time of release to the soil is the basic parameter of operation in terms of duration and coverage of the nutritional needs. The encapsulated material, being degraded in the soil, releases carbon and hydrogen to the micro-organisms of the soil, contributing to the development of biological activity, which is a second element of the activity of the encapsulated species in the soil.

The technique of formation of the encapsulated materials and of the encapsulation of products is a simple and effective process. The selected encapsulated material is heated to 170 degrees Celsius, thus coming into a molten state. At this temperature, materials which are stable at such temperature are added, such as phosphoric, sulphuric, potassium fertilisers and some pesticides and insecticides-pesticides. The remaining materials are added at lower temperatures up to 100 degrees Celsius, depending on their stability. The mixture flows to a pelletiser system wherefrom the products are collected in the form of granules which are packaged and can be marketed. A system of a controlled crusher can be also used in the flowing material, wherefrom the products are collected in a predetermined size distribution and can be also marketed.

The special colophon is an important element, a key-material for the composition of the encapsulation for maintaining the cohesion and the resin nature in the mixture and for promoting other desirable properties to it as well. The stability in water of an encapsulating material containing linear paraffin 33-40%, non linear paraffin 30% , polyethylene resin 17% and special colophon 3- 10% has been studied, along with the release of materials in (a) fertilisers 20-20-10 and (b) crushed aspirin (acetylsalicylic acid)

Table

Release of materials and Effect of the special colophon

Time (hours)	Quantity of Colophon / Release of materials					
	% content of colophon in the mixture					
	3%		5%		10%	
	(a)	(b)	(a)	(b)	(a)	(b)
10	-	-	5	(8)	10	(15)
20	-	(15)	10	(15)	25	(28)
30	20	(30)	35	(42)	50	(55)
60	40	(52)	55	(60)	80	(85)
90	60	(70)	80	(85)	100	(100)

(a) Fertiliser; (b) acetylsalicylic acid .

The inventors has studied the biological degradation of the encapsulating material in the soil in the presence of a product developed by themselves that binds water inside its molecule and renders the presence of water permanent for maintaining the biological activity in the soil.

The biological degradation starts from the special colophon, following which ruptures in the system occur leading to the cut-of and the discharge of the contents. The parts that are cut - off consist of resins which encapsulate a quantity of material which is slowly discharged with the biological degradation of the resin bearing it.

Thus, the release of the material to the soil is continuous in a time determined by the initial biological degradation and by the continuing biological degradation of the resins which exhibits great differentiation, hence the encapsulating mixture features short release times and long yield times, by design.

In the case of pesticides, insecticides, fungicides and other materials provided by spraying, the addition of the suitable encapsulating material in their solutions, which as already mentioned is polyethylene resin, effective protection is achieved at a 1/10 - 1/20 content of active material for environmental protection and for maintaining quality in the food chain.

Example No 1

Production of encapsulated fertilisers

a) Production of 20-10-5 fertiliser for use in gardens and greenhouses

Thirty (30) kg. Of an encapsulating mixture (of a composition of: 45% linear paraffin, 35% non linear paraffin ,10% stearine and 10% special colophon) are introduced to a reactor which features strong stirring and heating capacity and are heated to 170 degrees Celsius. At this temperature, and under strong stirring the addition of 70 kg of fertiliser starts (of a composition: urea 40 kg, potassium polyphosphate 21.7 kg, potassium sulphate 8.3 kg). The potassium polyphosphate and the potassium sulphate start being added at 170 degrees Celsius, but the temperature is gradually lowered to 120 degrees Celsius and the addition of urea starts, while maintaining the temperature to 110 to 120 degrees Celsius. The molten phase is then driven to a pelletizer wherefrom it is collected in granular form and packaged.

b) Production of 5-15-10 fertiliser for use in fruit bearing trees

Thirty (30) kg of an encapsulating mixture is added to the reactor (of a composition: polyethylene resin 45%, linear paraffin 10%, non linear paraffin 40% and special colophon 5%). The mixture is heated to 170 degrees Celsius and at this temperature the addition of 70 kg of fertiliser starts (composition: urea 12.6 kg, potassium polyphosphate 36.6 kg and potassium sulphate 20.6 kg) with the polyphosphate being added prior to the sulphate and then after stirring at 120 degrees Celsius, the addition of urea is effected under strong stirring. The molten phase is driven to a pelletiser), collected and stored in granular form.

c) Fertiliser 5-15-5 for use in reforesting

31.2 kg of an encapsulating mixture is introduced to the reactor (composition: polyethylene resin 45%, Asphalt 42% , non linear paraffin 7% , special colophon 5%) and is heated under stirring to 170 degrees Celsius. At this temperature, the addition of 68.8 kg of fertilisers under strong stirring (composition: urea 18.8 kg, diammonium polyphosphate 25 kg, potassium polyphosphate 10 kg and Potassium sulphate 15 kg). Potassium polyphosphate and Potassium sulphate are added first, whereas the diammonium polyphosphate and the urea are added when the temperature drops to 110 - 120 degrees Celsius under strong stirring. The molten phase is discharged to a pelletiser, collected in granules and stored.

Example No 2

a. Three hundred (300) grams of encapsulating material is introduced to a pilot unit under stirring and heating (composition: linear stearine 55%, linear paraffin 30% and special colophon 5%) and

is heated up to 130 degrees Celsius. At this temperature, weed killer is added in a ground form, the whole material is mixed and finally the molten phase at a temperature of 110 - 120 degrees Celsius is discharged to a pelletizer where it is shaped in spheres, collected and stored.

b. Three hundred (300) grams of encapsulating material is introduced to a pilot unit (composition: polyethylene resin 40%, polyethylene oxide resin 40%, linear paraffin 15% and special colophon 5%). The mixture is heated to 120 degrees Celsius and is melted and a ground mixture of insecticides is added to it under stirring and the formed mixture is passed to a pelletiser where it is shaped in granules and packaged.

c. Three hundred (300) grams of encapsulating material is introduced to a pilot unit(composition: polyethylene resin 30%, polyethylene oxide resin - 40%, linear paraffin 25% and special colophon 5%) and is heated to 120 degrees Celsius. Seven hundred (700) grams of ground fungicide are added to the mixture and the new mixture deriving is discharged to a peletiser where it is shaped in granules and stored.

Example No 3

Three hundred (300) grams of encapsulating material is introduced to a pilot unit (composition: stearine 75%, linear paraffin 20%, special colophon 5%) and is heated up to 130 degrees Celsius so that it is fully molten. Seven hundred (700) grams of ground aspirin (acetylsalicylic acid) is added to and the deriving is discharged to a pelletizer where it is shaped in small spheres and packaged.

CLAIMS

1. Method of production of encapsulated medicines, weed killers, fungicides, insecticides, fertilisers, pesticides and other materials for which a controlled use is required, in an encapsulating material which provides a biologically controlled slow yield of the encapsulated substances with complete consumption, with an encapsulating material consisting of resins of a predetermined biological degradation up to 80-98% and by special polymerised colophon of the pinus halepensis variety up to 2-20% .

2. Method according to claim 1 where the resins of the encapsulating material are linear paraffin, non linear paraffin, polyethylene resins, polyethylene oxide resins, stearines and asphalts with a given biodegradability and a melting point between 70 - 130 degrees Celsius

3. Method according to claim 1 where the special polymerised colophon which forms part of the encapsulating material is a colophon of the Pinus Halepensis variety

4. Method according to claim 1 where the encapsulating material is heated up to 170 degrees Celsius and the materials are added to the molten phase in a series depending on their stability whereas the temperature is gradually lowered to 100-120 degrees Celsius.

5. Method according to claims 1 and 4 where the encapsulated materials flow into a pelletiser system where they finally take the form of granules or are discharged to a special crusher unit where they are collected in a granular form and from final

marketable products with a stability for storage up to 60 degrees Celsius.

6. Method according to claims 1, 2,3, 4 and 5 where the encapsulated materials are fertilisers and soil pesticides and trace elements slowly and steadily released to the soil with the biological degradation of the encapsulating material with full nutritional coverage and complete consumption.

7. Method according to claims 1, 2, 3, 4 and 5 where the encapsulated materials are medicines for internal use by humans where the medicines are by design consumed slowly and completely, without side - effects.

8. Method according to claims 1,2,3,4 and 5 where the encapsulated materials are medicines for animals completely consumed without side - effects

9. Method according to claims 1,2,3,4 and 5 where the encapsulated materials are pesticides, insecticides, fungicides sprayed in a solution or powder form, where effective addition to the substrate is promoted with minimisation of their use complete consumption without rejection to the environment.

10. Method according to claims 1 to 9 where the encapsulating material is completely degraded biologically and provides carbon and hydrogen to the recipient substrate which constitutes biological strengthening and activation.

INTERNATIONAL SEARCH REPORT

Inte ɔnal Application No
PCT/GR 99/00003

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 B01J2/00 A01N25/26 C05G3/00 A61K9/28

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 B01J A01N C05G A61K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 3 252 786 A (BOZELLI ET AL.) 24 May 1966 see column 1, line 15 - line 26 see column 4, line 22 - column 5, line 37; claims 1-15; example I; tables I,II	1-6,8-10
Y	US 5 137 563 A (VALKANAS GEORGE N) 11 August 1992 see the whole document	1-6,8-10
A	WO 97 46075 A (VALKANAS GEORGE N) 11 December 1997 see the whole document	1-6,9,10

-/--

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

"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 claim(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 when the document is taken alone

"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.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
19 April 1999	27/04/1999

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Cubas Alcaraz, J

1

Form PCT/ISA/210 (second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

Inte onal Application No
PCT/GR 99/00003

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
A	DATABASE WPI Section Ch, Week 9503 Derwent Publications Ltd., London, GB; Class A97, AN 95-016465 XP002100205 & JP 06 279161 A (KOREA RES INST CHEM TECH), 4 October 1994 see abstract	1,6,10
A	EP 0 305 918 A (AIR PROD & CHEM) 8 March 1989 see claims 1-6	1,2,6-10

1

Form PCT/ISA/210 (continuation of second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

Information on patent family members

Inter nal Application No
PCT/GR 99/00003

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 3252786 A	24-05-1966	FR 86770 E	
		FR 1400375 A	24-09-1965
		FR 1450420 A	28-11-1966
		GB 984109 A	
		NL 6409862 A	25-11-1965
		US 3301656 A	31-01-1967
US 5137563 A	11-08-1992	NONE	
WO 9746075 A	11-12-1997	GR 1002633 B	03-03-1997
		AU 2911997 A	05-01-1998
EP 0305918 A	08-03-1989	US 4891223 A	02-01-1990
		CA 1330942 A	26-07-1994
		DE 3876724 A	28-01-1993
		DK 490788 A	04-03-1989
		ES 2052656 T	16-07-1994
		JP 2069414 A	08-03-1990
		JP 8025870 B	13-03-1996
		NO 178486 B	02-01-1996