A NOVEL PROCESS TO MANUFACTURE GRANULAR PESTICIDES

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Introduction

The utilization of granular pesticides has been increasing rapidly during the past decades. This is due to the numerous advantages of the granular form: entrainment of the particles by air currents will be less and hence the danger of dispersal will be reduced, the pesticide will reach the surface of the soil or the water even through dense foliage. Therefore such preparations can be used for protection against noxious insects and weeds in the development stage of cultivated plants when spraying will no more be effective. The active ingredient will be set free slower from the particles, so that the action will be prolonged. Simpler machines are required for spreading, no water is necessary at this operation and the particles will get exactly to the place where desired. Furthermore, the handling of granular pesticides is safer [1].

High-grade granular pesticides, containing the active agent or the combination of active agents in amounts corresponding to the tolerance limit, must satisfy many requirements, such as:

a) the particles shall be equal in mass, finely dispersed, homogeneous and free of dust,

b) the particles shall be free-flowing, preferably spherical in shape,

c) their mechanical strength shall be satisfactory,

d) the active agent shall be stable in the presence of the support and binding materials, and

e) the rate of setting free the active agent shall be suitable [2].

Theory and experimental

Several methods have been developed to manufacture granular pesticides with properties favourable to satisfy requirements. Numerous variants of each method exist [3, 4].

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1. *Direct impregnation.* A granular support is prepared previously by some means and the solution of the active agent is sprayed on it. Subsequently the product is further ground.

2. *Impregnation with a suspension.* Active agents poorly soluble in water and in organic solvents, which therefore cannot be applied with Method 1, are sprayed in form of a suspension on the granular support. This is followed by grinding of the product.

3. *Adhesive method.* An improved development of Method 2, with several variants. *a)* After application of the suspension according to Method 2, the solution of an adhesive is sprayed on the product. *b)* First, the adhesive solution is sprayed on the support, and the active agent is subsequently applied in powder form. *c)* A modification of the procedure *b)* after application of the active agent, a second layer of the adhesive solution is sprayed on the product. Subsequent grinding of the product is used in all variants.

4. *Post-drying technique.* The water-soluble active agent is sprayed on the granular support and cautiously dried. Subsequently a further layer is sprayed on, followed by repeated drying. The technique is used when a single application of the solution would not be capable to ensure the required concentration of the active agent in the product.

5. *Vacuum evaporation.* The essence of the method consists in the application of vacuum to evaporate the solvent during the impregnation of the support with the solution of the active agent, and in the subsequent recovery of the solvent. The method is used when the solvent is expensive, the active agent is poorly soluble or when the solvent is phytotoxic.

6. *Melt process.* The granular support is impregnated with the melt of the low-melting, non-volatile active agent. Impregnation is carried out e.g. in rotating drums, and followed by cooling and post-grinding.

7. *Extrusion process.* The active agent is mixed with the support substance in powder form and with the solution of a binder. The mass is granulated in an extruder and the granules are submitted to drying. The process yields cylindric, compact particles. Similar processes pass the mass through a screen to form granules. The method is suitable to prepare support particles.

8. *Agglomeration technique.* The mixture of the active agent and the support in powder form is fed into a rotating drum or pan, and the solution of the binder is sprayed on under constant rotation of the equipment. A widespread variant of this technique is fluidizing aggregation of the powder-like particles. The granules obtained are spherical in shape and largely porous. The method is suited to prepare support particles.

9. *Briquetting process.* The active agent, the support material and the binder solution are mixed, briquettes are moulded under pressure, dried, and the blocs are subsequently crushed to the desired particle size. The granules

thus obtained are irregular in shape and compact. The method is suited to prepare support granules.

The cited methods allow to prepare granular pesticides from various active agents, production costs varying according to the process. However, in certain cases, for instance for liquid active agents with high vapour pressures, none of the processes will yield products satisfying all requirements at economically acceptable cost.

The shape of the granules obtained by the processes 1—6 depends on the shape of the support, on the manner of application and on the effect of post-grinding. Since close to spherical supports can usually be obtained only by Method 8, which yields porous structures, the granular pesticides prepared according to processes 1—6 are also largely porous and in many cases unsatisfactory regarding mechanical strength. The active agent is usually deposited on the surface of the support. If the vapour pressure of the active agent is high, the volatile substance may eventually be set free already before application, during storage. It is scarcely possible to plan the rate at which the active agent will be set free, and hence to foresee the period of its activity. The only process allowing such control is Method 3, if the active agent and the binder are applied alternately in several layers, utilizing in this manner the delaying effect of the binder layers. However, this process is costly and wearisome.

In view of mechanical strength, extrusion and similar processes (Method 7) and briquetting (Method 9) are favourable, due to the compact structure obtained, but spherical products cannot be achieved by these means.

The different variants of the agglomeration technique (Method 8) yield spherical particles, but, besides yielding porous products, have the further disadvantage that they usually require higher than ambient temperatures, so that volatile active agents will be out of question.

To eliminate the mentioned disadvantages, we attempted to develop a novel technique, the so-called suspension method.

Our research work disclosed that if we applied a volatile active agent or a mixture of active agents to a powder-form support with high sorption capacity, e.g. bentonite, diatomite, organophilic bentonite, cellulose powder, in amounts that the mixture still remain powder-like, then add gypsum to the powder, submit the mixture to homogenization, and subsequently homogenize it with water or with a dilute solution of a water-soluble polymer, e.g. polyvinyl alcohol, methyl cellulose, polyvinylpyrrolidone, degradated starch etc., a homogeneous paste will be obtained. By introducing the paste into an organic liquid (preferably containing a small amount of a surface-active agent) like e.g. silicone oil or paraffin oil in which the components of the paste are insoluble, and submitting the system to slow stirring, a suspension containing regular spherical-shaped particles will be formed. The size of the particles will depend, on the one hand, on the intensity of stirring, and on the other hand, on the interaction between the liquid and the paste, which can be controlled by the nature and amount of the surface-active agent contained in the liquid. In the course of stirring, the product hardens, and after some time it will become filterable. Subsequent washing and drying will yield a granular product consisting of mechanically strong, regular spherical-shape an uniform grain-size particles. No further crushing or grinding is needed.

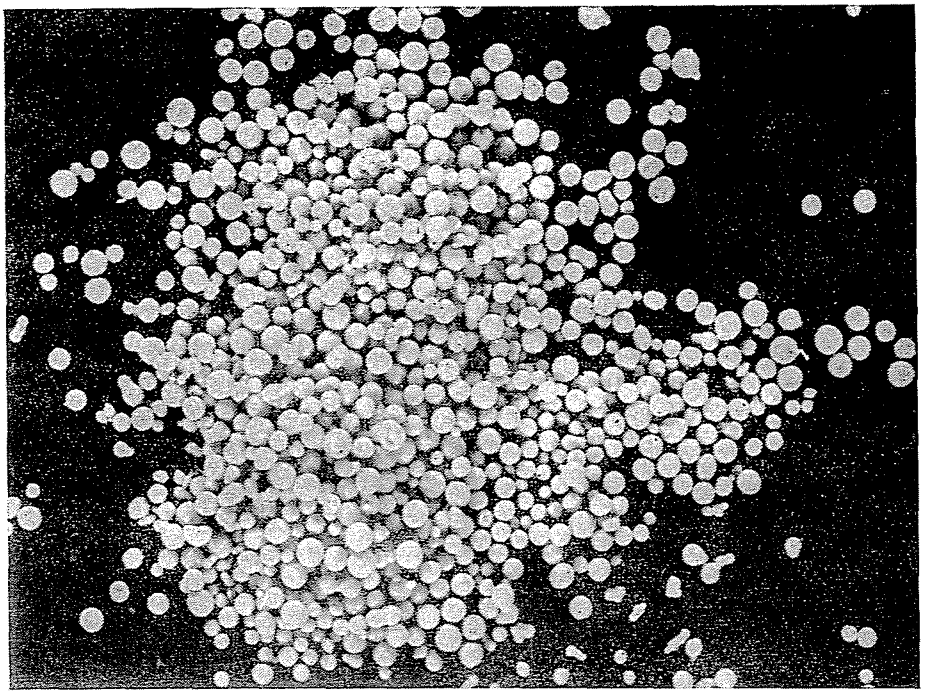

Fig. 1. Microgranules containing EPTC, prepared with the suspension process

The process takes place at ambient temperature, if necessary, even below (but above zero °C). By increasing the temperature, hardening of the particles will be accelerated.

A microphotograph of a granular pesticide prepared by the suspension method is shown in Fig. 1.

Further experimental work demonstrated that granular material containing an active agent can also be obtained

a) by applying the active agent in solution on the powder-like support and subsequently evaporating the solvent,

b) by mixing the active agent in the melted state with the powder-like support, followed by cooling and — if necessary — crushing, *c)* by mixing the solid active agent with the powder-like support. In this case the latter need not have excellent adsorption properties, poorer adsorbents like kaolin or talc will do,

d) by omitting the powder-like support and using only solid, powder--like active agent,

e) by bonding the active agent by using the solution of some polymer to the support which is no adsorbent,

f) by applying the active agent to a powder-like support made capable of binding it by a previous treatment with the solution of some polymer,

g) by applying various active agents simultaneously or successively, using any of the processes *a)* to *f)*.

In our experiments we used the liquid herbicide EPTC (N,N'-dipropyl--1-thioethylcarbamate) and the solid herbicide Propachlor (N-isopropyl-α--chloroacetoanilide) as active agents. The total content of active agents in the granular product was 10% in all cases.

For rating the granular products, we determined — among others — average grain size and grain size distribution by screen analysis, mechanical strength from the weight loss of the material submitted to an abrasion test by agitation for 8 hours under specified conditions, and the rate of setting free the active agent from the product.

Setting free of the active agent was tested *in vitro* in distilled water at 20 °C (5 g product in 1000 cm^3 water). To follow the dissolution of the active agent we took a sample of 40.0 cm^3 daily for a period of at least 20 days, making up the initial volume with water. The concentration increase in the samples was followed by gas chromatography of the extract of the aqueous solution samples. In the given examples, we applied *n*-hexane for EPTC and xylol for Propachlor as solvents for extraction. The effect of dilutions were accounted for by correction factors.

The kinetics of the dissolution of the active agent from the granular pesticide could be approached by the first-order equation C *vs.* t

$$C = C_0[1 - e^{-k_0 t}] \qquad (1)$$

where C_0 is the saturation concentration in water of the active agent at the test temperature and k_0 is the first-order rate constant of the dissolution. To characterize the rate of liberation, we used the most probable value of k_0, calculated by computer from the experimental values, which yielded the minimum deviation between the percentage values in the experimental and calculated C *vs.* t curves.

By comparing the k_0 values of granular pesticides with identical concentrations of the active agent(s), but differing in composition, we stated that the rate constant of the liberation of the active ingredients depends substantially

— on the nature of the powder-like support,

— on the relative ratios of the components (active agent, powder-like support, gypsum and water or polymer dissolved in water),

— on the amount and nature of the dissolved polymer added to the paste, and

— on particle size and surface area.

These statements are illustrated by some experimental data listed in Table 1.

Table 1

Granular pesticides prepared by the suspension method: $k_0 \cdot \text{day}^{-1}$ values. Nominal active agent content: 10% EPTC, particle size 0.63 . . . 1.6 mm

Support material	Ratio of support to gypsum	Binder	Binder content of solution, %	$k_0 \cdot 10^2$ day^{-1}
Bentonite	0.50	Methyl cellulose	0.4	3.5
Bentonite	1.25	Methyl cellulose	0.4	3.4
Bentonite	3.50	Methyl cellulose	0.4	1,8
Bentonite	3.50	Polyvinyl alcohol	0.4	2.8
Bentonite	3.50	Methyl cellulose	1.2	3.7
Diatomite	3.50	Methyl cellulose	1.2	5.0

By varying the above conditions, it becomes feasible to plan the manufacture of such granular products whose capacity of setting free the active agent will be adapted best of all to the requirements of the application in question.

In conclusion, the advantages of the suspension granulating process developed by us can be summarized as follows:

(i) Independently of solubility conditions, the process can be applied to solid and liquid active agents and to mixtures of active agents.

(ii) Granulation can be carried out at ambient temperature or even lower temperatures in a single operation. It is hence suitable to granulate liquid active agents with high vapour pressures.

(iii) The product is very uniform, the degree of dispersion can be regulated simply, by varying the intensity of stirring or by choosing an appropriate type of stirrer.

(iv) The granules are spherical in shape, and the product is free-flowing.

(v) The products are compact, their mechanical strength is excellent.

(vi) The rate of setting free the active agent, and thus the period of action, can be deliberately controlled between certain limits.

A patent has been applied for the process [5].

Summary

A novel process for manufacturing granular pesticides is described. The suspension method allows to obtain regular spherical-shaped, compact particles with excellent mechancal strength, which set free the active agent at a rate controllable within certain limits. This ate depends on the parameters of the manufacturing process.

References

1. Summzer, B.: Internat. Pest. Control, **5**, 6 (1963)
2. Stonov, L.: Nachrichtenblatt für den deutschen Pflanzenschutzdienst, **10**, 194 (1967)
3. Van Valkenburg, M.: Pesticide Formulations. Marcel Dekker Inc. New York, 1973
4. Andriska, V.—Bozzay, J.: Növényvédőszer készítmények technológiájának alapjai (Principles of Manufacturing Pesticide Products). BMETI, Budapest, 1978
5. Hungarian Patent Application

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