

Pesticide formulations and process for the manufacture thereof

The invention relates to pesticide aqueous suspensions containing beta-cypermethrin as insecticide active ingredient in 0.1 to 20 % by mass beside physical and chemical stabilizers. Further subject of the invention is a process for the preparation of these suspensions.

Beta-cypermethrin (The Pesticide Manual 9th Edition p 212-213) is approximately a 2:3 mixture of the following enantiomer pairs: (S)- α -cyano-3-phenoxy/benzyl-(1R)-cis-3-(2,2-dichlorovinyl)-2,2-dimethyl/cyclopropane/carboxylate and (R)- α -cyano-3-phenoxy/benzyl-(1S)-cis-3-(2,2-dichlorovinyl)-2,2-dimethyl/cyclopropane/carboxylate with (S) - α - cyano - 3 - phenoxy/benzyl- (1R) -trans -3-(2,2-dichlorovinyl)-2,2-dimethyl/cyclopropane/carboxylate and (R)- α -cyano-3- phenoxy/benzyl-(1S)-trans-3-(2,2-dichlorovinyl)-2,2-dimethyl/cyclopropane/carboxylate in the form of trielin cristalls. It is a well known, very effective insecticide introduced to the market by CHINOIN Pharmaceutical and Chemical Works Co. Ltd. in 1989 under the name of CHINMIX.

Beta-cypermethrin, its synthesis and compositions containing beta-cypermethrin as active ingredient are described in Hungarian patent specification Nr. 198.612, European patent specification Nr. 0208758, USA patent specifications Nos. 5.192.739 and 5.153.349 and in the British patent specification Nr. 2.251.621.

The above mentioned patents describe procedures for the formulation of beta-cypermethrin where the active ingredient is dissolved in organic solvent(s), preferably in the presence or without the presence of emulsifiers. The product thus obtained will be sprayed out preferably emulsified in water. The manufactured and marketed preparations are all organic solutions of the active ingredient (Chinmix 5 EC, Chinmix ME, Cyperyl-S ULV).

Such preparations have beside their indisputable advantages (simple manufacturing, good stability and easy handling) several disadvantageous characteristics resulting mainly from the use of organic solvents. These are: fire and explosion danger, high toxicity, expensive packaging.

All these disadvantages can be eliminated if the active ingredient is formulated in an aqueous suspension. This way the easy handling and by using the appropriate formulation technology the biological effectiveness of the product equivalent to that of the solvent formulations can be preserved.

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In aqueous suspension concentrates (known in plant protection as FW or SC formulations) the active ingredient is present in a fine (usually in a few μm size) colloidal state. Physical stability of the system is ensured by surface active substances, antifreeze substances, thickeners and other auxiliaries substances. The extremely low particle size is achieved by wet grinding with the help of pearl mills.

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To prepare a stable aqueous suspension is not an easy task even for a technician. The colloid system is in a very sensitive equilibrium and can be influenced by several factors such as temperature, interactions among the elements of the system, etc.

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Physical and chemical characteristics of the suspendable substance (active ingredient) have a great significance and therefore there is no universal formulation recipe which could be applied for any active ingredient. Technicians generally accept it as a basic requirement that the substance to be formulated should be practically water insoluble, should have a relatively high melting point and should be resistant to hydrolysis.

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Beta-cypermethrin meets partly these requirements because its water solubility at 20°C is 0.01 mg/litre and with addition of certain substances (e.g. maleinic acid, malonic acid, phthalic acid) its chemical stability can also be insured.

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The difficulty had lain in its relatively low (60 to 65°C) melting point which caused the failure of the early formulation trials. Although the temperature of the suspension during usual grinding processes did not quite reach 60°C (generally it was between 35 to 50°C) the active ingredient partly still melted or recrystallized.

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The reason for this phenomenon is complex but it can be explained partly by the liberation of local energy formed on collision and friction points of the grinding bodies (pearls), partly by the plastification (melting point decreasing) effect of surfactants.

It was our aim to find such auxiliary substances which eliminate the above mentioned disadvantageous effects, have easy accessibility and are compatible with other components of the suspension system.

5 In the course of our experiments we found that certain water insoluble silicates such as kaolin if ground together with beta-cypermethrin inhibit its melting and recrystallization, moreover decrease the tendency to settling which is characteristic of pyrethroid preparations in aqueous suspensions with low (2 to 5 % by mass) active ingredient concentration.

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In the course of our experiments we have found surprisingly that beta-cypermethrin is inclined to recrystallization if stored at higher temperature in spite of its extremely low water solubility (0.01 mg/l 20°C). This phenomenon can be explained by increased water solubility of the active ingredient at higher temperature, which solubility can be
15 further increased by the solubilizing effect of surface active substances. Growing particle size is an unfavorable phenomenon in the suspension because as a result of this the biological effectiveness and physical stability of the product may decrease. In the course of our formulation experiments we tried to inhibit the growth of the suspended particles and we found that this goal can be achieved by application of
20 certain synthetic, amorph silicic acids (e.g. Wessalon S).

As we mentioned earlier in order to insure chemical stability of beta-cypermethrin, that is to inhibit undesired epimerization, different organic acids are used. In the course of our experiments we were able to find such substances which chemically
25 stabilize beta-cypermethrin and at the same time possess good dispersing and wetting effects both during grinding and application of the product. In addition they protect well the particles of the active ingredients and inorganic auxiliary materials against changes e.g. agglomeration during storage.

30 These surface active and physicochemical stabilizer compounds are ethoxylated polyaryl-phenol-phosphates or sulfates and from these ethoxylated tristyryl-phenol-phosphates proved to be very useful especially those that contain 16 moles of ethoxy groups.

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Aqueous suspensions of pesticides according to our invention contain the following components:

0.1-20 % by mass beta-cypermethrin

0-40 % by mass other pesticide substances

5 1-10 % by mass surface active substances in total and within this

1-5 % by mass ethoxylated polyaryl-phenol-phosphate or sulfate

0.1-25 % by mass mineral and/or synthetic silicates

0.1-1 % by mass synthetic silicic acid and

to make up to 100 % by mass with other auxiliary material(s) and water as dispersant.

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Under other active ingredients, compounds may be considered whose target of application and the time of application coincide with that of beta-cypermethrin, are compatible with other components of the formulation of the invention and can be formulated in stable aqueous suspensions. In a wider sense these active ingredients
15 may be pesticides, growth regulators, adjuvants, repellents, attractants and synergizing substances.

Beside the already mentioned ethoxylated polyaryl-phenol-phosphates and sulfates other dispersing and wetting substances may be used as surface active substances
20 such as lignin sulfonates, ethoxy-propoxy block copolymers, condensed aromatic sulfonic acids, ethoxylated alkyl phenols, aromatic alkyl sulfonic acids, ethoxylated fatty alcohols, etc.

As mineral silicates kaolinites and aluminum silicates may be used. Suitable thickeners are e.g. polysaccharides (e.g. xanthan-gum) and cellulose ethers. As antifreeze substances e.g. ethylene or propylene glycol may be used. Formaldehyde or 1,2-benzisothiazoline-3-on may be suitable conserving agents against microbial degradation of thickener polysaccharides. For example potassium hydroxide, sodium carbonate or triethanolamine can be used as organic or inorganic bases. Useful
25 antifoaming agents are silicon emulsions.

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The compositions of the present invention are pesticides with excellent physical and chemical stability which can be sprayed diluted with water or undiluted, may be used

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as a seed coating substance alone or together with other treating agents and they can also be used in insect traps together with attractants or alone.

5 In the following examples we illustrate the compositions and manufacturing processes of the present invention without limitation of our patent claim:

EXAMPLES

10 **Example 1: Preparation of a pesticide formulation containing 5 % by mass of active ingredient**

The formulation is prepared in two steps. First a more concentrated (15 % by mass active ingredient) suspension is made which is diluted to 5 % by mass by addition of auxiliary substances.

15 3 parts of ethoxylated tristyryl-phenol-phosphate dispersing agent and 0.6 parts of silicon defoamer are dissolved in 64.3 parts of water. To the solution 15 parts of beta-cypermethrin insecticide active ingredient, 15 parts of kaolin and 2.1 parts of synthetic silicic acid are added under vigorous agitation and the coarse suspension obtained is grinded in a pearl mill to average particle size of 2 µm. The
20 fine suspension thus obtained is diluted three times of its mass by adding additional components according to the following:

To 100 parts of the suspension 133.7 parts of water, 6 parts of ethoxylated tristyryl-phenol-phosphate and 30 parts of triethanolamine 30 parts of glycol and 30 parts of 2
25 % Xanthan-gum solution are added.

The following composition is obtained:

	beta-cypermethrin	5.0 % by mass
	ethoxylated tristyryl-phenol-phosphate	3.0 % by mass
30	kaolin	5.0 % by mass
	silicic acid	0.7 % by mass
	propylene glycol	10.0 % by mass
	xanthan gum	0.2 % by mass

triethanolamine

0.1 % by mass

water

76.0 % by mass

The product is a suspension of grayish white color. Its density is 1.05 g/cm³ at 20°C.

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Example 2

The product prepared according to example 1 was stored at 45°C for 1 month and for 1 year in a warehouse in the open without heating and its physico-chemical characteristics were measured. Results are listed in Table 1.

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Table 1

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Storage conditions	Average particle size	Upper separation	Sediment	Active ingredient (%)		
				Total	cis(S) isomer	trans(S) isomer
Before storage	1.2 µm	0	0	4.97	1.98	2.99
2 weeks at 45°	1.7 µm	0	0	4.92	1.97	2.95
1 month at 45°C	1.7 µm	trace	0	4.94	1.89	3.05
1 year in warehouse	1.9 µm	0	0	4.99	1.97	3.02

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Example 3: Biological efficacy on house-fly laboratory

Quantities of 0,5 ml tart solution made by serial dilution were sprayed onto the bottom of Petri dishes (9 mm diameter) by using Potter-tower (Potter, C. Annals of Applied Biology, 39:1-28)

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After drying 10-10 2-4 day-old adult female house flies (*Musca domestica*, WHO/SRS strain) were placed in the Petri dishes, which were then covered.

The flies recovered within half an hour. Mortality was assessed after 24 hour-exposition on deposit.

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Control treatments were done with tap water only. Tests were performed in three parallels and repeated at 2-5 occasions.

LC₅₀ values were calculated from dose-mortality relationships by probit-analysis (Labware, Probit analysis, CompuDrug, Budapest)

Results are listed in Table 2.

Table 2.

Formulation	Active ingredient	n ¹	Slope ²	SE ³	LV50 ⁴	SE ⁵
					ppm	
Chinmix 5 EC	beta-cypermethrin	720	1.52	0.11	14.2	1.2
Fendona 10 FW	alpha-cypermethrin	540	1.31	0.12	12.2	1.3
Chinmix 5SC	beta-cypermethrin	540	1.70	0.13	8.2	0.7

¹Number of treated flies used to the calculation of LC50

²Slope of log-concentration and probit-mortality

³Standard error of the slope

⁴Equipotential concentration

⁵Standard error of LC50

Data of the Table show that the efficacy of Chinmix SC prepared according to example 1 is significantly higher than that of Chinmix 5 EC containing the same active ingredient or that of Fendona 10 FW containing alpha-cypermethrin.

Example 4: Biological efficacy on Colorado beetle in field test.

Comparative field tests of Chinmix SC prepared according to example 1 and standard Chinmix 5 EC formulations were done on Colorado beetle adults (*Leptinotarsa decemlineata*).

Treatments were carried out on the 4th of August using backpack spraying machine with 500 l spraying solution. Area: 100 m². Repetition: 4 in each dose.

Efficacy was assessed at 1, 5, 9 days after treatment by counting living insects on 5x4 designated stems per lot. Efficacy was calculated by Henderson-Tilton formula.

Results are shown in Table 3.

Formulation	Dose (l/ha)	% Efficacy (Henderson-Tilton)		
		Day 1	Day 2	Day 3
Chinmix 5 EC	0.35	48.5	68.6	38.0
Chinmix 5 SC	0.30	88.3	79.1	61.5

Results of the Table show that also a lower dose of Chinmix SC is significantly more effective on Colorado beetle imagos than that of the EC-formulation.

What we claim is:

1.

An aqueous suspension containing

5 0.1-20 % by mass beta-cypermethrin

0-40 % by mass other pesticide substances

1-10 % by mass surface active substances in total and within this

1-5 % by mass ethoxylated polyaryl-phenol-phosphate or sulfate

0.1-25 % by mass mineral and/or synthetic silicates

10 0.1-1 % by mass synthetic silicic acid and

up to 100 % by mass other auxiliary materials and water as dispersant.

2.

15 Aqueous suspension according to claim 1 containing as ethoxylated polyaryl-phenol-phosphate, ethoxylated tristyryl-phenol phosphate with 16 EO-unit.

3.

Aqueous suspension according to claim 1 containing kaolin as silicate.

20 4.

Aqueous suspension according to claim 1 containing as surface active substance 1-5 % by mass non-ionic surfactant, preferably ethoxylated suspension according to claim 1 containing as other auxiliary substance 0.1-1 % by mass thickener, preferably xanthan gum, 5-20 % by mass antifreeze substance preferably propylene glycol, basic
25 compound(s) preferably triethanolamine, 0.1-1 % by mass antifoaming agent, preferably silicone type defoamer, 0.01-1.0 % by mass preserving substance, preferably formaldehyde.

5.

30 Process for the preparation of an aqueous suspension according to claim 1 characterized by grinding beta-cypermethrin together with mineral and/or synthetic silicates, being used in an amount close to the amount of beta-cypermethrin and with ethoxylated polyaryl-phenol-phosphate or sulfate and synthetic silicic acid.



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(21) International Application Number: PCT/HU96/00020 (22) International Filing Date: 19 April 1996 (19.04.96) (30) Priority Data: P 95 01147 24 April 1995 (24.04.95) HU (71) Applicant (for all designated States except US): CHINOIN GYÓGYSZER ÉS VEGYÉSZETI [HU/HU]; Termékek Gyára Rt., T6 u. 1-5, H-1045 Budapest (HU). (72) Inventors; and (75) Inventors/Applicants (for US only): SZÉKELY, István [HU/HU]; Krajcár u. 6, H-2120 Dunakeszi (HU). BOTÁR, Sándor [HU/HU]; Regényes u. 5, H-1221 Budapest (HU). BERTÓK, Béla [HU/HU]; Ják u. 44/a, H-1221 Budapest (HU). HAJIMICHAEL, Janis [HU/HU]; Regényes u. 5, H-1221 Budapest (HU). KIRÁLY, Jenő [HU/HU]; Puli sétány 6, H-1213 Budapest (HU). HADOBÁS, Jánosné [HU/HU]; Vajda Péter u. 9, H-1089 Budapest (HU). PAP, László [HU/HU]; Vadon u. 19, H-1112 Budapest (HU). MÉNESINÉ, B., Ildikó [HU/HU]; Damjanich u. 4/a, H-8200 Veszprém (HU).		(74) Common Representative: CHINOIN, Gyógyszer és Vegyészeti; Termékek Gyára Rt., Iparjogi Osztály, T6 u. 1-5, H-1045 Budapest (HU). (81) Designated States: AL, AM, AT, AU, AZ, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IS, JP, KE, KG, KP, KR, KZ, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, US, UZ, VN, ARIPO patent (KE, LS, MW, SD, SZ, UG), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published <i>Without international search report and to be republished upon receipt of that report.</i>
(54) Title: PESTICIDE FORMULATIONS AND PROCESS FOR THE MANUFACTURE THEREOF (57) Abstract The subject of the invention is an aqueous suspension containing: 0.1-20 % by mass beta-cypermethrin, 0-40 % by mass other pesticide substance, 1-10 % by mass surface active substances in total and within this, 1-5 % by mass ethoxylated polyaryl-phenol-phosphate or sulfate, 0.1-25 % by mass mineral and/or synthetic silicates, 0.1-1 % by mass synthetic silicic acid and up to 100 % by mass other auxiliary materials and water as dispersant.		