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Environmental Aspects Of Using Microencapsulated Malathion.

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ABSTRACT

Research on the development of environmentally friendly forms of microencapsulated pesticides are among the most promising and sought-after areas of science and technology. The paper presents the results of research of microencapsulated malathion. These biological and toxicological studies indicate that the microencapsulation several times increases the duration of the effective action of the said insecticide and reduces its toxicity, which allows transferring it from the second group, according to the sanitary classification (toxic), to the fourth (low-toxic). Optimum permeability of microcapsules as long-acting polymer diffusion systems allows for release of insecticides in minimal doses, harmless to humans and the environment in general.

Keywords:microencapsulation; plant protection products; malathion;prolonged action; environmental safely.

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INTRODUCTION

Due to the success in creating the polymer materials with special functional properties the polymer systems and the controlled release devices started intensively developing currently. Such systems, when placed in the appropriate environment, release a substance according to the preset concentration-time program [1,2].

One of the variants of release systems are microcapsules (MC) which enclose a capsulated substance in a polymer shell serving as a membrane releasing the substance by diffusion mechanism.

Objectives, methodology and research design: We used malathion [o,o-dimethyl-s-(1,2-dicarbethoxyethyl) dithiophosphate] in the development of environmentally friendly microencapsulated forms as an active substance, which is used in agriculture for the control of harmful insects, mites and pests of food products, in medical, sanitary and household pest control in veterinary medicine for combating endo- and exo-parasites of animals and birds, and for the destruction of flies and mosquitoes in livestock premises [3].

Creating the sustained-action is related to the study of the permeability of the microcapsules, where the active substance release can be controlled by varying the thickness and permeability of the surface of polymeric membranes [4].

Achieving optimal release regime is associated with the establishment of the kinetic parameters of the process [5]. To study the release process of the microcapsules, we applied the derivatographic method under dynamic conditions. This method is based on a combination of the differential thermal analysis (DTA) and the differential thermogravimetric analysis (DTGA).

The properties of the used components of microencapsulation polycondensation reaction were investigated by IR-spectroscopy in the range of 3400-700 cm^{-1}.

The biological efficacy of the microencapsulated forms was studied in greenhouse conditions according to standard procedure. Toxicity was determined on experimental animals by administering the test substance in the gastrointestinal tract. We estimated local irritating action to the skin and mucous membranes of the eyes, as well as skin-resorptive effect.

Discussion of the research outcomes: To study the permeability, the o-xylene microcrystals (malathion concentrate solvent [6]) were used as a test sample, with an average size of about 20 microns with polyurea shells (Fig. 1).

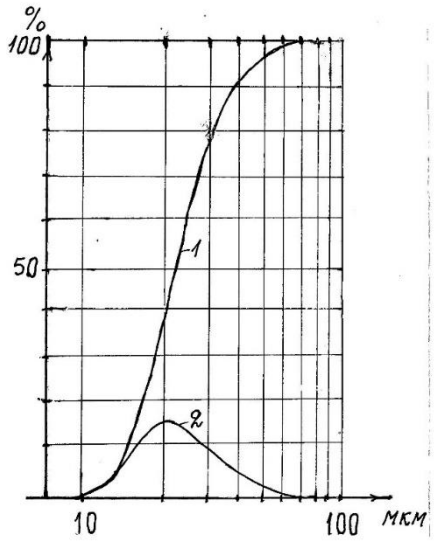

Fig. 1. Integral (1) and differential (2) curves of o-xylene MC distribution by size.

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Granulometric indicators (volume distribution, average size, specific surface area) were determined by laser diffraction. the obtained derivatograms (Figure 2) were processed by Reich method [7] with the determination of the maximum release rate and the corresponding parameters. At the same time, the mass loss rate and the residual mass of substance were calculated, and the diagram of lgR_t versus B was plotted, which is equal to:

$$B = [(W_{max}/T^2_{max} \cdot R_{max}) \cdot lgW \cdot (1/2.3 \cdot T)] \cdot 10^4 \text{ , where}$$

R_t- mass loss rate, mg/deg; W_{max} – residual mass of substance, corresponding to the point of extremum; R_{max} – rate at the point of extremum;
W – residual mass of substance at appropriate temperature;

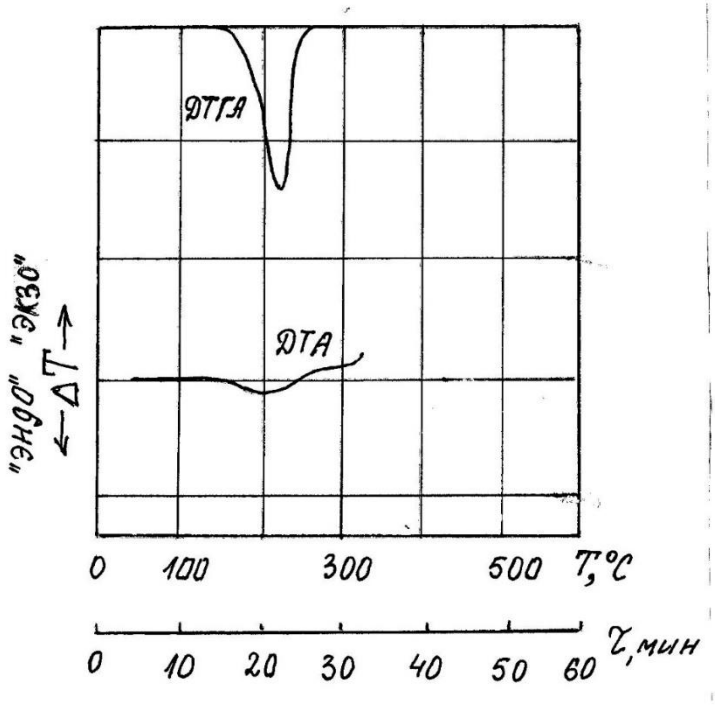

Fig. 2. DTA and DTGA curves of the microcapsules with o-xylene mass fraction of 85%.

The activation energy value was determined by the formula: $E_a = tg\phi \cdot R$,

where R – universal gas constant; ϕ - inclination angle of line (Figure 3);

The reaction order n and pre-exponential factor A were calculated by the formula:

$$n = (E_a/R) \cdot [W_{max}/(T^2 \cdot R_{max})]$$
$$lgA = lgR_t - (E_a/R) \cdot [lgW \cdot W_{max}/(T^2_{max} \cdot R_{max}) - 1/(2.3 \cdot T)]$$

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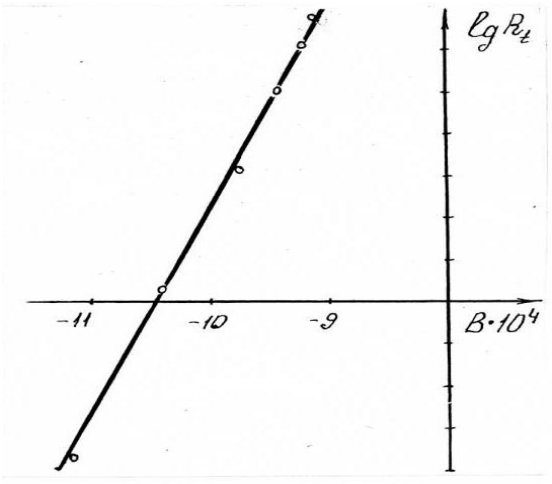

Fig. 3. R_t to B diagram for microcapsules with o-xylene mass content of 85%.

The values of kinetic parameters (Table 1) indicate that the activation energy of o-xylene release is close to its vaporization enthalpy ($\Delta H_{vap.}$ = 36.8 kJ/mol).

Table 1: Kinetic parameters of o-xylene release from MC

Parameter	Value
Reaction order, *n*	0.13
Pre-exponential factor, *LgA*	5.07
Activation energy, *E* (kJ/mol)	40.72

The reaction order, close to zero, indicates a constant release rate of o-xylene. We can assume that this is due to the capillary condensation of the saturated vapor of o-xylene in the MC, providing for the release of the encapsulated substance in strictly dosed portions.

Using the well-known equation: $ln\ (k_M/k) = -\ E/R\ (1/T_M - 1/T)$, we can calculate the duration of release of o-xylene from the microcapsules at different temperatures.

The resulted findings are consistent with the results of thermogravimetric studies of MC permeability under isothermal conditions [8] for toluene microcapsules, for which the volatilization of the solvent occurs at a constant rate. This indicates the reaction order of evaporation, which is close to zero. *lg W* -1/*T* diagram is shown in Fig. 4.

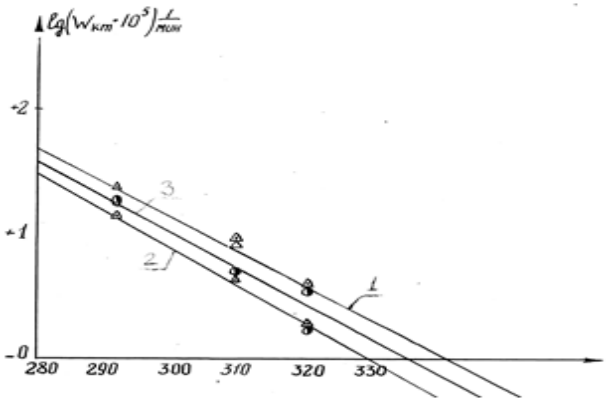

Fig. 4. The dependence of the mass loss rate on the temperature in capsules in lgW_{const} - 1/*T* coordinates: 1 - fraction of 1.0-2.0 mm; 2 - fraction of 0.25-0.50 mm; 3 - fraction of 0.50-1.00 mm;

As can be seen, this dependence is expressed by straight lines. The activation energy is calculated from the slope in these coordinates, and is equal to ~ 41.9 kJ/mol. This value is close to the evaporation heat of toluene ($\Delta H_{evap.}$ = 44.0 kJ). Apparently, this dependence is due to the vapor pressure of the solvent, which depends not on its quantity, but on the temperature. By extrapolating a straight line in $lgW - 1/T$ coordinates, we can estimate the permeability of the MC (Figure 4) at the application temperature.

The studies of the permeability-dependent biological activity of microencapsulated forms of malathion included the preparation of primary formulations based on microcapsules with polyurea shells of different composition for the subsequent determination of optimal compositions during biological tests.

Microencapsulation by interfacial polycondensation was carried out using a polyisocyanate and a polyethylene polyamine for production of polyurea shells. The composition of the components of polycondensation reaction was investigated by IR spectroscopy [9].

The used polyisocyanate was a mixture of 2,4- and 4,4-diphenylmethane diisocyanate:

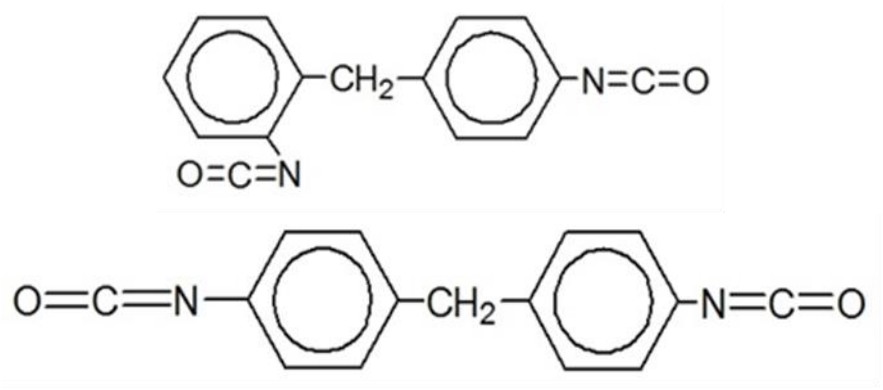

Figure 5 shows the IR spectrum of polyisocyanate in the range of 2500-700 cm^{-1}.

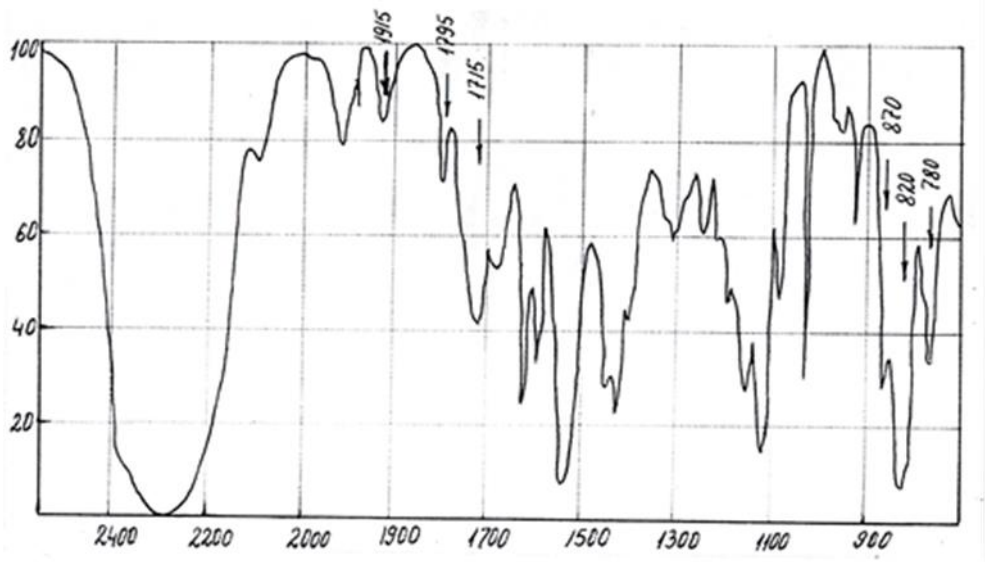

Fig. 5. Polyisocyanate IR spectrum

Polyethylene polyamine is a mixture of amines, which amine part includes ethylene diamine, diethylenetriamine, 1,2-aminoethylpiperazine, the main of which is the ethylamine. Poly-ethylene polyamine was studied in comparison with the nitrogen subjected to hydrochlorination for its protonation. IR spectra of samples in the range of 1800-1700 cm^{-1} are shown in Fig. 6.

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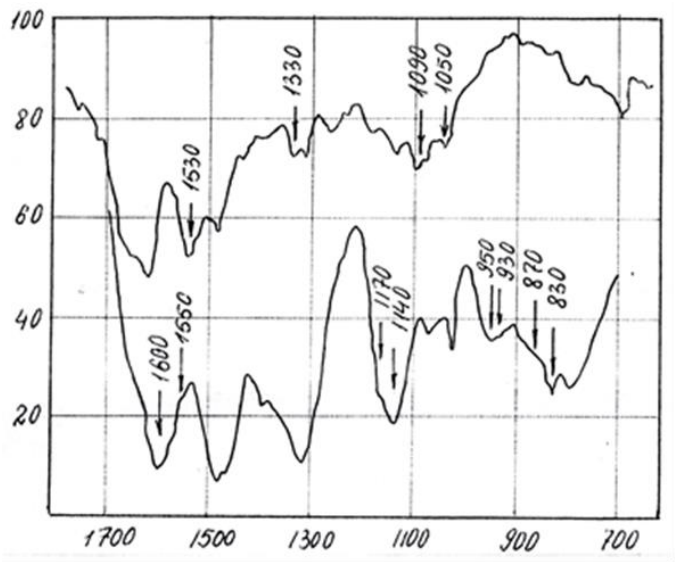
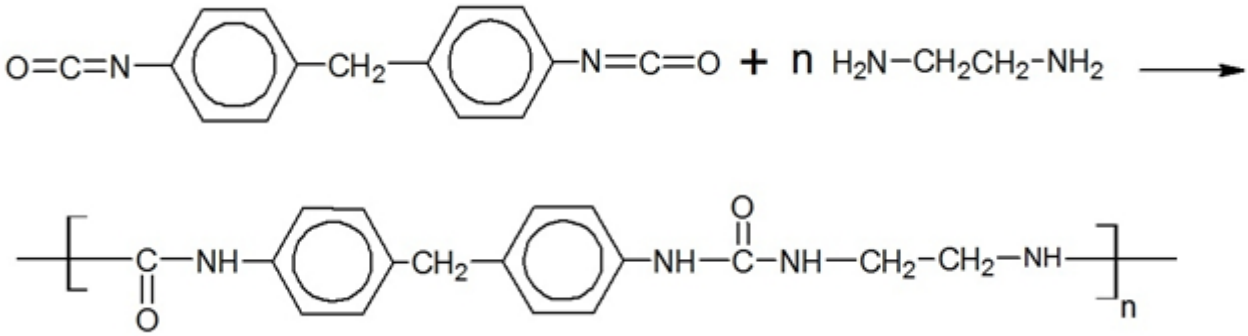


Fig. 6. Polyethylene polyamine IR spectrum: 1 - protonated; 2 –non-protonated.

The absorption spectrum of the polyurea (Fig. 7), obtained with the use of the above monomers, first of all, has no bands of monomeric isocyanate (2290-2280 cm^{-1} and 1400 cm^{-1}), which is, obviously, due to their complete exhaustion [10]:



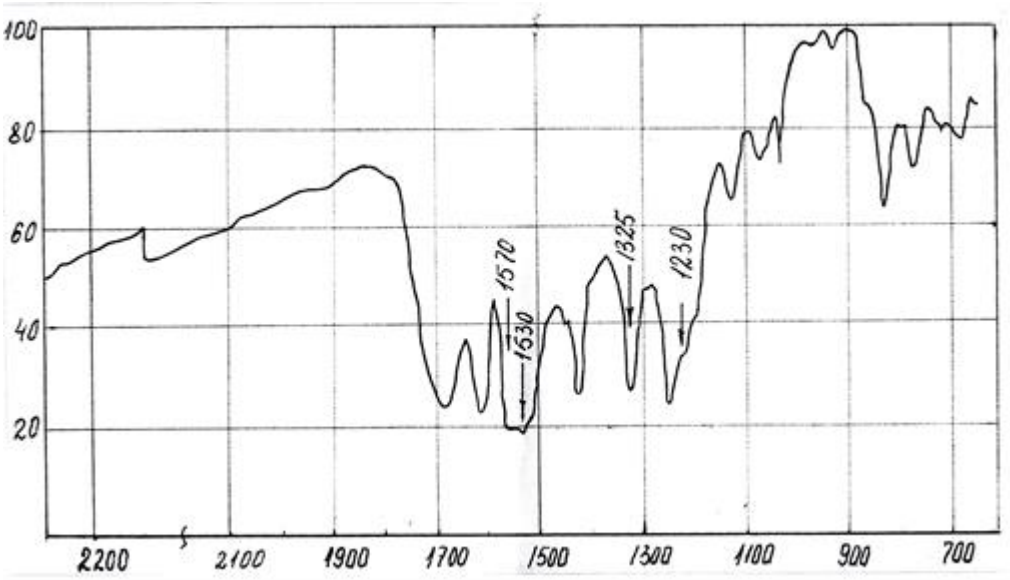


Fig. 7. Polyurea IR spectrum

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Malathion samples were tested for biological activity in the micro-encapsulated form in comparison with emulsion. Microencapsulated form was an aqueous suspension of microcapsules with a volume-average radius of 30±20 microns with polyurea coatings, and the emulsion form was an aqueous dispersion of insecticide.

The content of main components in the microencapsulated form compositions is shown in Table 2.

Table 2: The content of main components in the microencapsulated form compositions

No	Component name	Mass fraction, %				
		1	2	3	4	5
1.	Malathion	13.44	11.04	6.03	3.90	2.63
2.	Polyurea	1.47	4.94	6.81	9.46	13.38

The presented microencapsulated malathion forms were tested in greenhouse conditions against aphids by the standard method [11].

Results of biological tests are shown in Table 3 in comparison with the standard (emulsion form). Treatment was carried out with the formulations at malathion concentration of 0.012% of active ingredient.

Table 3: Biological test results of the formulations of microencapsulated malathion

Formulation No.	Aphids mortality in % on accounting days							
	1	5	6	7	8	12	13	14
1	90.6	72.5	71.7	70.0	67.5	76.7	38.3	35.0
2	48.1	51.2	76.7	55.0	63.3	63.3	25.0	-
3	36.4	38.7	45.0	7.5	-	-	-	-
4	4.2	-	-	-	-	-	-	-
5	3.1	-	-	-	-	-	-	-
Standard	97.3	5.0	-	-	-	-	-	-

More clear dynamics of aphid mortality on first accounting days is shown in Table 4.

Table 4: Biological test results of the formulations of microencapsulated malathion

Formulation No.	Aphids mortality in % on accounting days			
	1	2	3	5
1	90.6	76.2	70.0	72.5
2	48.1	81.2	76.2	51.2
3	36.4	67.5	55.0	38.7
4	4.2	16.2	11.6	-
5	3.1	17.5	10.0	-
Standard	97.3	11.2	8.3	5.0

As follows from the above data, the duration of the protective effect of microencapsulated forms of malathion against aphids increases with a decrease in polyurea shell thickness (compounds 3, 2, 1). Formulations 4 and 5 are low-active. The efficacy of malathion upon its microencapsulation (formulations 1, 2) increased during day 1 to 12 in comparison with a standard.

Formulations 1 and 2 were used in toxicological tests [12]. Toxicity evaluation was conducted on mice, rats and rabbits by administering the formulation to the stomach, applying on the skin and mucous membranes of the eyes in acute experiments. The experiment was conducted on mature female albino mice

with a total weight of 20±3 g, and female rats with a total weight of 200±20 g. Each test group included six test and six control animals. Data on DL_{50} are presented in Table 4.

Table 4: Toxicity of the microencapsulated malathion formulations

Formulation No.	DL_{16}, mg/kg		DL_{50}, mg/kg		DL_{84}, mg/kg	
	mice	rats	mice	rats	mice	rats
1			12250±1043	7950±759		
2	6300.0	6500.0	12950±1075.0	10834±739.0	14500	12900

We revealed the following clinical pattern of toxic action: difficult breath, depression, weakness. Application of the formulations to the dorsal skin of rabbits to investigate skin-irritating effect resulted in hyperemia, disappearing in 3 days. Application of 50 mg formulations to the mucous membranes of eyes caused weak hyperemia for 2 days.

Acute experiments generally indicate similar toxicity of formulations No. 1 and 2. DL_{50} indicators allow us to classify the formulations as the fourth group of toxicity according to hygienic classification of pesticides (low toxic), whereas DL_{50} of emulsion malathion is 1082±160 mg/kg for rats, and 1583±260 mg/kg for mice (second group of toxicity). As can be seen, microencapsulation of malathion reduces its toxicity by 7-10 times.

CONCLUSION

Thus, the adjustment of the MC permeability by changing the thickness, surface and permeability of the polymeric shells provides optimum release rates.

The results of biological and toxicological tests indicate the possibility of achieving high efficiency of the microencapsulated forms for a long period, as well as safety of organophosphate pesticides by their microencapsulation.

Microencapsulation ensures an increased duration of insecticide action by several times at the same application rate with the achievement of minimal doses of insecticides providing, on the one hand, the persistence of effective protection from pests, and, on the other hand, their reduced toxicity, making the drugs safer to human and farm animals. At the same time, reduced frequency of plant treatment leads to a reduction in environmental burden on the soil and the environment in general.

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