

EFFECT OF PARTICLE SIZE DISTRIBUTION ON THE STABILITY OF PESTICIDE SUSPENSIONS

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Summary

The effect of particle size distribution and milling time on the stability of suspension-type pesticide formulations was studied for two pesticides being at the development stage at the North Hungarian Chemical Works: Tricomb 40 FW (active agents: propachlor, terbutryne and atrazine) and Terbutrin 40 FW (active agent: terbutryne). Optimum milling time was found to be ~90 min with Tricomb; with Terbutrin — for the applied system of additives — milling time should not exceed 30 minutes.

Milling trials should be performed with each new formulation before commercialization, since proper selection of particle size may be of great importance not only from the view of stability, but also from the view of potential energy savings.

Introduction

Formulations of pesticides as concentrated aqueous suspensions (FW) became much widespread in recent years, since they have the following advantages as compared to traditionally formulated products (powders, WP, granular pesticides) [1]:

— they allow much more accurate and economic application of the target area,

— consequently, more expensive pesticide types may be introduced,

— FW formulations are easy to handle, since they can be measured by volume and no dust is formed at dilution.

The concentrated suspensions are prepared by wet milling; they contain 30...60% active agent, with sizes of the dispersed particles in the range of 0.1...5 μm .

The requirement to FW products is that they should be stable during storage for several years at changing temperature conditions, that is, the

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properties of the system must not change noticeably after a fixed time. It is of importance from the view of application that relatively small amounts of material must be spread uniformly over a large area.

To achieve a satisfactory pesticide formulation, it is hence necessary to establish a stable space structure in the dispersion operation of the active agent, which will prevent the dispersed particles to stick to one another or to sediment. This space structure must remain unimpaired at all temperatures to which the product may be subjected; it must, however, be satisfactorily fragile to relatively slight shear stresses in order to disperse spontaneously when diluted with water.

The general conditions of the physical stability of concentrated suspensions are known from the literature. They are summarized in Table 1 (from Tadros [2]).

As indicated in Table 1, physical stability of concentrated suspensions is attained by various additives, covering the surface of the dispersed particles and establishing structure in the system.

The stabilizing effect of various additives has been dealt with extensively in the literature [3–13]. Relatively little has, however, been reported on the

Table 1

General conditions of the physical stability of concentrated suspensions

Condition of stability	Effects by which it can be satisfied
No irreversible coagulation	Repulsion of the double layer: adsorption of ionic tensides. Such systems are, however, sensitive to the presence of electrolytes Steric repulsion: adsorption of nonionic tensides or macro-molecules. This allows to tolerate reasonable amounts of electrolytes Combination of electrostatic and steric repulsion: polyelectrolytes
No scale formation	Controlled coagulation Satisfactorily stable structure of the suspension by additives of organic polymers, inorganic dispersed systems (clay or oxides or both)
Reduced crystal growth	Use of less soluble and more stable polymorphic forms Additives hindering crystal growth
Spontaneous dispersion at dilution	No irreversible coagulation Weak coagulates readily dispersible at mild impact Formation of a not too rigid structure in the system

particle size distribution of the suspensions. Generally it is only the usual size range that is marked out. But it appears obvious that given additives in a given amount can only stabilize the system, if the specific surface area of the dispersed particles is in proportion to the amount of additive. Hence, it is a fundamental condition for preparing concentrated suspensions to produce systems with adequate degrees of dispersion. Adequate degrees of dispersion are not equivalent to the finest particle size range that can be achieved with the given mill, since adhesion forces or electrochemical coagulating forces always acting between the particles cannot be compensated by raising the degree of dispersion above a certain limit. For every concentrated suspension, an optimum limit value of particle size exists, below which it is senseless to mill, and rather, in many cases, it has an adverse effect, since it may lead to excessive cohesion forces. On the other hand, mills consume about 10^3 – 10^4 times as much energy as the “useful” energy calculated from the free surface energy produced in milling. The efficiency of milling is affected — besides energy consumption of the mill — by the physical and chemical characteristics of the material to be milled and by the nature of the dispersion medium and of the additives. For this reason, as a final step in the formulation of all concentrated suspensions, it is indispensable to establish milling conditions, that is, particle size ranges, that will ensure optimum stability of the product. In the followings, the milling studies carried out with two FW pesticides under development at the enterprise Északmagyarországi Vegyiművek will be described.

Experimental

The investigated products were both herbicides: (Aktinit FK) Tricomb 40 FW, with propachlor, atrazine and terbutryne as active agent, and Terbutrin 40 FW, with terbutryne as active agent. Their active agent content is 40%; in addition, they contain 3% milling additive and about 10% tensides and thickener. The dispersion medium is a mixture of water and ethylene glycol.

From the view of formulation, Tricomb is more difficult to handle, since it contains more components, and the solubility of propachlor in water is fairly significant. For this reason, Tricomb developed in the R + D laboratory of Északmagyarországi Vegyiművek is of the rigid-type, that is, in order to maintain stability, the enterprise made concessions to spontaneous dispersion at dilution.

We prepared all samples by dissolving the tensides in the appropriate amount of a mixture of water and ethylene glycol, using a whip stirrer, and subsequently added the pre-milled active agents and milling additives. 250 g of the sample were then milled with 350 g glass balls 1 mm in diameter at 1500 rpm for different periods. The thickener was added to the milled product.

Table 2
Milling time of samples

No. of sample	Name	Milling time, min
1	Tricomb	3
2	Tricomb	20
3	Tricomb	40
4	Tricomb	60
5	Tricomb	90
6	Tricomb	120
7	Tricomb	150
8	Terbutrin	3
9	Terbutrin	20
10	Terbutrin	30
11	Terbutrin	40
12	Terbutrin	60
13	Terbutrin	90
14	Terbutrin	120
15	Terbutrin	150

Milling times for the samples are listed in Table 2.

The herbicide suspensions were then subjected to particle size analysis, centrifugal sedimentation and drop test. No rating based on collective sedimentation was feasible, since the samples practically did not sediment during standing, they belonged to the class of coherent-structure suspensions.

Results and discussion

Results of particle size analysis

Particle size distribution of the samples identical in composition, but differing in milling time was determined immediately after their preparation, using a Sartorius 4600 type sedimentation balance [14]. The concentrated suspensions were diluted with water (19° German hardness 190 mg CaO/dm³) to about 1% solids content, since this concentration approaches that of dilute herbicide sprays.

The sedimentation rate curves of the Terbutrin samples are shown in Figs 1 and 2. They are of interest insofar as for milling times of 40 min and more, the curves are markedly S-shaped, indicating coagulation. This phenomenon is presumably caused by the fact that the tensides present are unable to stabilize the increased surface area formed by milling; they will slowly be desorbed, and adhesion forces will come to the fore. To confirm this assumption, we prepared

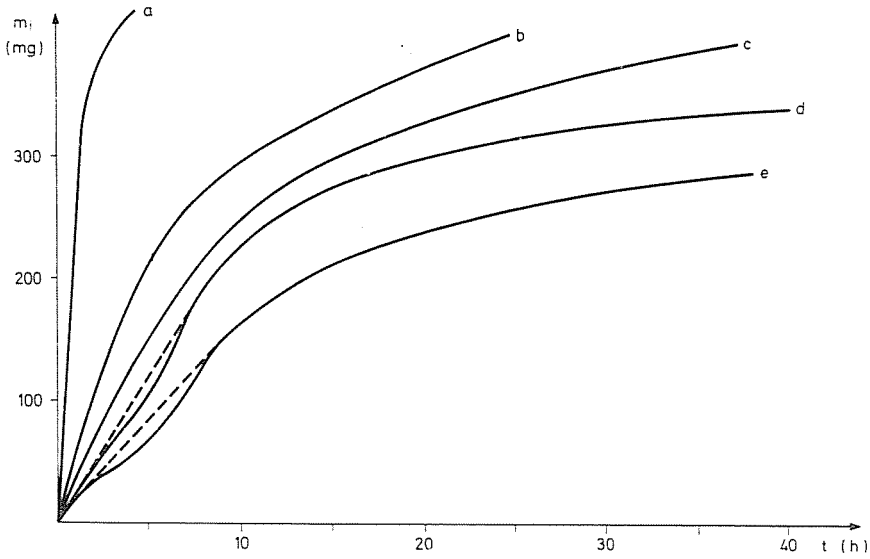


Fig. 1. Sedimentation rate curves of Terbutrin samples: a — 3 min milling (Sample 8); b — 20 min milling (Sample 9); c — 30 min milling (Sample 10); d — 40 min milling (Sample 11); e — 60 min milling (Sample 12)

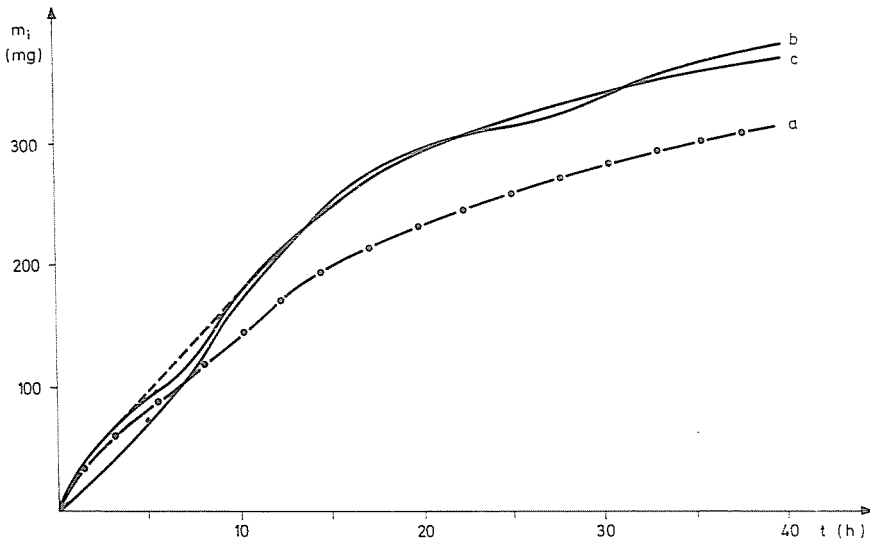


Fig. 2. Sedimentation rate curves of Terbutrin samples: a — 90 min milling (Sample 13); b — 120 min milling (Sample 14); c — 150 min milling (Sample 15)

a Terbutrin sample with 12% instead of 10% of tensides and milled it for 40 minutes. In fact, this product did not coagulate when diluted.

The granulometric curves could not be constructed from those sedimentation rate curves that indicated coagulation having taken place. The granulometric curves of the three non-coagulated Terbutrin samples and of the sample prepared with 12% of tensides are presented in Fig. 3, indicating that the half-value of size distribution (i.e. the diameter higher than that of 50% of the particles) for 30 min milling time (Sample 10) is 5.8 μm , and the sample contains practically no particles with diameters exceeding 15 μm , whereas the

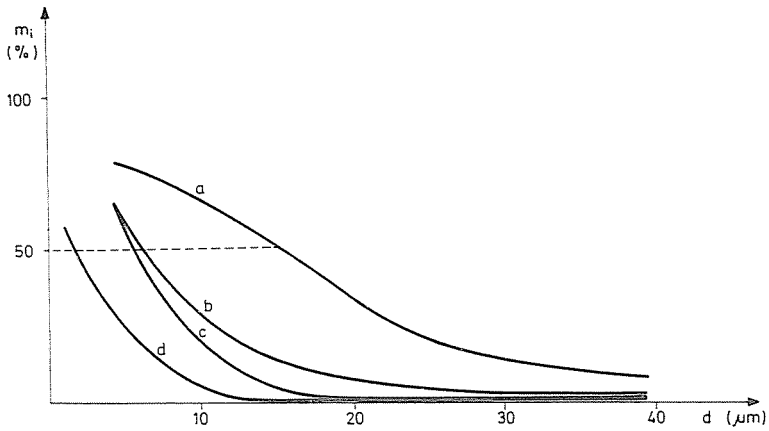


Fig. 3. Granulometric curves of Terbutrin samples: a — 3 min milling (Sample 8); b — 20 min milling (Sample 9); c — 30 min milling (Sample 10); d — 40 min milling, sample containing 12% tensides

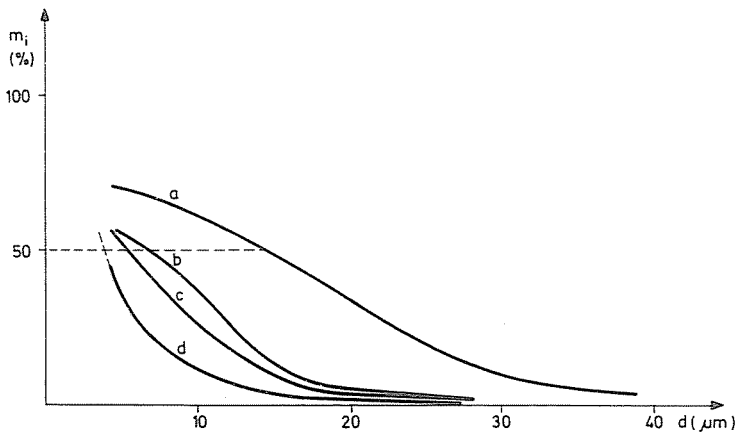


Fig. 4. Granulometric curves of Tricomb samples: a — 3 min milling (Sample 1); b — 20 min milling (Sample 2); c — 40 min milling (Sample 3); d — 60 min milling (Sample 4)

half-value of size distribution of the sample with 12% tenside is as low as $1.5 \mu\text{m}$, and the sample contains no particles larger than $10 \mu\text{m}$. In this case, it should be decided by the requirements of application whether it is expedient to increase the amount of tensides in the pesticide.

The particle size distribution curves of the Tricomb samples are shown in Figs 4 and 5, demonstrating reduced particle size with increasing milling time. The half-value of size distribution for the sample milled for 150 min (Sample 7, curve *c* in Fig. 5) is as low as $2.9 \mu\text{m}$, and the system contains no particles larger than $10 \mu\text{m}$.

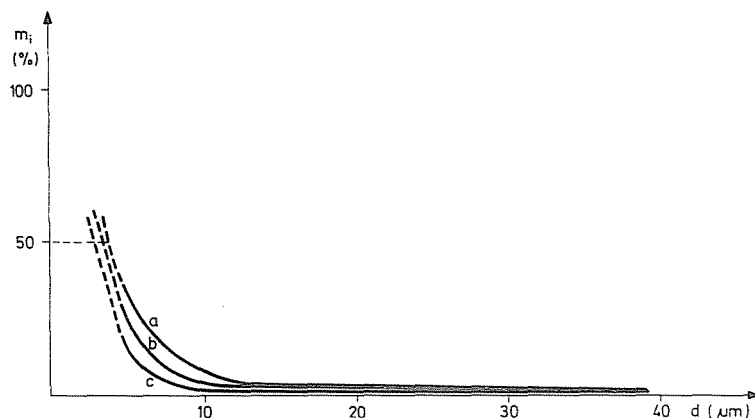


Fig. 5. Granulometric curves of Tricomb samples: a — 90 min milling (Sample 5); b — 120 min milling (Sample 6); c — 150 min milling (Sample 7)

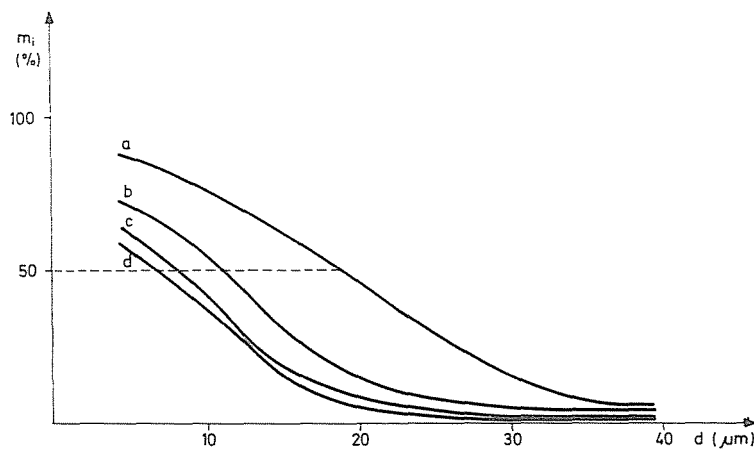


Fig. 6. Granulometric curves of Tricomb samples after two months storage: a — 3 min milling (Sample 1); b — 20 min milling (Sample 2); c — 40 min milling (Sample 3); d — 60 min milling (Sample 4)

After a two-month storage period we again determined particle size distribution in both series of samples. The curves for Tricomb are shown in Figs 6 and 7, those for Terbutrin in Fig. 8. Although the half-values of size distribution do not characterize distribution unequivocally, for comparison's sake their changes during the two-month storage period is presented in Fig. 9 (Tricomb) and Fig. 10 (Terbutrin).

From the granulometric results one may conclude that optimum milling time for the Tricomb samples is around 90 min, while for the Terbutrin samples milling time exceeding 30 min is not advisable, since it leads to over-milling,

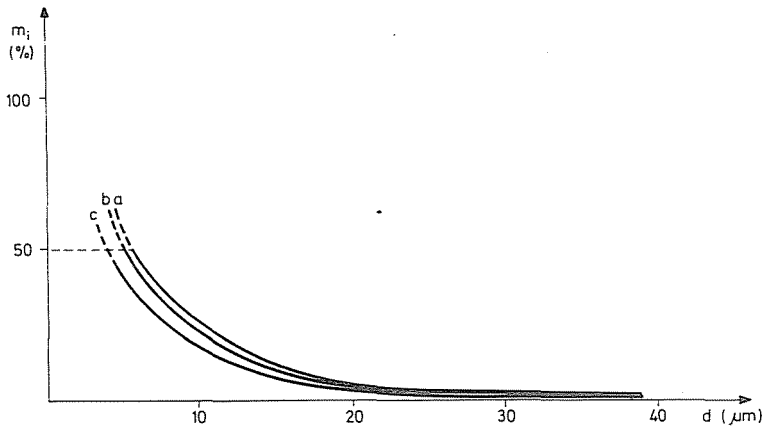


Fig. 7. Granulometric curves of Tricomb samples after two months storage: a — 90 min milling (Sample 5); b — 120 min milling (Sample 6); c — 150 min milling (Sample 7)

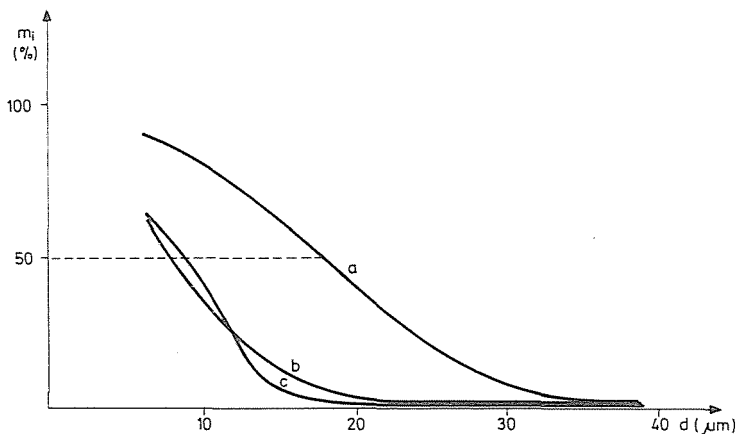


Fig. 8. Granulometric curves of Terbutrin samples after two months storage: a — 3 min milling (Sample 8); b — 20 min milling (Sample 9); c — 30 min milling (Sample 10)

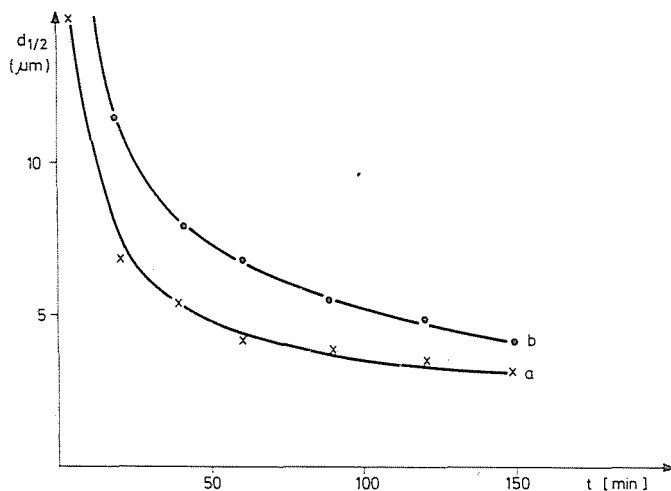


Fig. 9. Half-values of size distribution vs. milling time of Tricomb samples; a — immediately after preparation of the samples; b — after two months storage

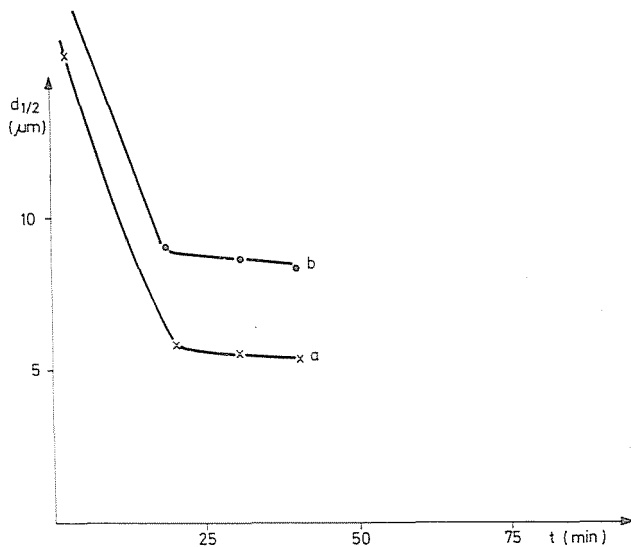


Fig. 10. Half-values of size distribution vs. milling time of Terbutrin samples; a — immediately after preparation of the samples; b — after two months storage

that is, the given system of additives is incapable to stabilize the sample, at dilution a slightly coagulated suspension will be formed.

The granulometric results after two months of storage demonstrate that one must reckon with the Ostwald ripening effect, and that — in conformity with the theory — the extent of crystal growth will be the lesser, the more homogeneous the distribution of particle size is.

Results of drop tests

This simple test technique was developed to present information on spontaneous dispersion of pesticide suspension at dilution.

A drop of known volume is dropped from a height of 0.5 cm onto the surface of a 20 cm high column of distilled water, and the behaviour of the drop is observed. The following cases may occur:

(i) The drop immediately disintegrates, when it comes into contact with the water surface. This is a proof that the suspension is readily dilutable. However, our experience showed that such samples are not satisfactory regarding their structure: fillers will rapidly sediment out and will frequently form cake.

(ii) As the drop passes downwards through the 20 cm water column, it gradually disperses. Such samples are still readily dilutable and possess satisfactory structures.

(iii) The drop does not disperse in the water column, it reaches the bottom without breaking up. Such pesticides are difficult to dilute. However, their strong, coherent structure protects them from settling out. Frequently the drops only fall out from the dropper if blowing is applied.

Chemists obviously aim at case (ii) in their formulations. However, if concessions must be made, type (iii) will be preferred to type (i), since with the

Table 3
Results of the drop test

No. of sample	Dropping conditions	Extent of dispersion of the drop
Tricomb		
1	Blowing required	No disintegration
2	Blowing required	No disintegration
3	Blowing required	No disintegration
4	Blowing required	No disintegration
5	Blowing required	Slight dispersion
6	Blowing required	The major part of the drop fell to the bottom without disintegration
7	Blowing required	No disintegration
Terbutrin		
8	Blowing required	Slightly dispersed
9	Drops spontaneously	Major part dispersed
10	Drops spontaneously	Major part dispersed
11	Drops spontaneously	Major part dispersed
12	Drops spontaneously	Major part dispersed
13	Mild blowing required	Slightly dispersed
14	Mild blowing required	Slightly dispersed
15	Mild blowing required	Slightly dispersed

high-performance agitators used in agriculture, dilution will be practicable, even though consuming more energy.

The results of the drop tests for both series of samples are summarized in Table 3. The results demonstrate that from the view of dilution, Terbutrin samples form more suitable suspensions. The Tricomb samples — owing to their coherent structure — fell out from the dropper only when blowing was applied, and remained practically undispersed.

In this test, Sample 5 proved best within the Tricomb series, while in the Terbutrin series Samples 9–12 were equally satisfactory.

Results of centrifugal sedimentation

By sedimentation in the centrifugal force field, accelerated storage is modelled. This testing technique is of importance particularly in plant quality control, since all other testing methods provide information on the stability of the product only after a longer period. However, the results obtained with centrifuging must be accepted with certain reserves only, since it may happen that accelerated sedimentation taking place at values of several hundred g breaks up the structure of feebly coagulated systems, which would not happen in the gravitation field of the earth. For this reason, many authors propose to use a maximum value of 4 g . However, centrifuges with such low acceleration values are not commercially available. We used a T-30 table centrifuge in our tests. From the amount of sediment formed at the higher g values, we could state whether the structural stability of the sample is satisfactory or not. The samples which completely disintegrate under the effect of centrifuging must be subjected to further tests allowing to find out whether coagulation of the system proceeded irreversibly or reversibly.

Table 4

Results of centrifugal sedimentation tests for Terbutrin samples

No. of sample	Milling time, min	Centrifuging conditions	
		Mass 20 g, 2000 rpm, 5 min	Mass 10 g, 3000 rpm, 10 min
Sediment, %			
8	3	18.2	26.6
9	20	17.0	26.6
10	30	13.7	22.3
11	40	14.1	25.2
12	60	9.3	19.7
13	90	13.4	20.5
14	120	13.8	21.3
15	150	17.2	22.3

The Terbutrin samples were tested at two sets of conditions: with samples of 20 g, at 2000 rpm, for 5 min, and with samples of 10 g, at 3000 rpm for 10 min. After centrifuging, we weighed the residue at fixed decantation conditions: the tubes were clamped at a 45° angle and held in this position as long as water dribbled from the sample.

The Tricomb samples, when subjected to centrifuging, did not sediment, but gelled.

The results of centrifugal sedimentation for the Terbutrin samples are summarized in Table 4, allowing the following conclusions to be made:

— formulation of the Terbutrin samples is satisfactory, the sedimented amounts may be considered realistic. Our experiences showed that samples prepared with poor formulation yield sediments of 35...70% at similar experimental conditions;

— rating by the centrifugal test demonstrates that the sample milled for 60 min is best;

— presumably, slight coagulation takes place in the sample milled for 150 min already in the concentrated state, weakening the structure of the system;

— the amount of the centrifuged sediment is characteristic above all for the structural stability of the system, since the amount of the sediment obtained e.g. from Sample 8 consisting of much coarser particles barely exceeds that of the other samples.

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