

THE STUDY OF DISSOLVING UREA GRANULES BASED ON THE GENERALISED DIMENSIONAL ANALYSIS

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ABSTRACT. This paper work contains the study of non-stationary dissolution of individual urea granules used as fertilizers. The present study is based on The Generalized Dimensional Analysis and includes comments about the fundamental factors, the important factors, the secondary factors and about the unimportant factors which can control the phenomenon. It also contains experimental determinations on simple and filmed urea granules that lead to a general equation for the dissolving process.

Keywords: *Generalized Dimensional Analysis, non-stationary dissolution, pure and filmed urea granules, mathematical equations for non steady-state dissolution.*

INTRODUCTION

Starting with The Generalized Dimensional Analysis Method (GDAM), defined by Prof. Dr. Eng. Staicu C-tin, [1] and later developed by others, [2], we tried to study the dissolution of urea granules utilized as fertilizers. According to the methodology, we established the list of variables, that can influence the process. The list is presented below:

$$\| \tau, D, d, c_{\text{sat}}, m, d, V, g, \rho, \eta, \nu \|$$

where:

- L, M, T - the symbols of the measuring units for Length, Mass and Time;
- $Fo_d = (\tau D_{di})/d^2$ - the Fourier criteria for diffusion, [-];
- $Sc = (\nu/D_{di})$ - the Schmidt criteria, [-],
- $k_1, k_2, k_3, k_4, \dots$ - the numerical coefficients of the monomial relation, [-].

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Table 1. The parameter's exponent of variables

The parameter's exponent	The parameter, (variable)
a	τ , - dissolution time, [s];
h	D_{di} , - diffusion coefficient, [m ² /s];
b	c_{sat} , - concentration at saturation, [kg/m ³];
e	m, - the mass of particle, [kg];
i	d, - the diameter of particle, [m];
f	V, - the volume of particle, [m ³];
p	g, - the gravitational acceleration, [m/s ²];
t	ρ , - the solvent's density, [kg/m ³];
r	η , - dynamic viscosity, [kg/m·s];
s	ν , - kinematic viscosity, [m ² /s];

The working procedure is detailed in the bibliographical references [1, 2] and in others as well [3, 4, 5]. The linear matrixes of the minimum parameters that can influence the variables with direct action over the process are separated by the variables that have a reverse action over the process. The undetermined dimensional system of the variables exponents is attached to this linear matrix. This truncated system is resolved by the progressive homogenization method. The solution to this system must be: minimal, integer, positive and nonzero. The variables are introduced one by one and the computation procedure is repeated for each case. The numeric value of the parameters exponent and the number of solutions accepted by the GDAM establish the level of hierarchization of the parameter, from fundamental to unimportant. The monomial expression of the distributed variables is formed with the numeric value identified for each parameter's exponent. In order for a monomial expression to be correct it must be dimensionally homogenous and the numeric value of the monomial's coefficient must be constant. Through common mathematical operation the similitude criteria or simplexes can be obtained, offering new possibilities for interpretation to each parameter's importance.

a) The study starts with the minimum number of variables that can possibly influence the dissolving process. The linear matrix with dimensional matrix of the variables attached to it is:

$$\begin{array}{l}
 \mathbf{L} \\
 \mathbf{M} \\
 \mathbf{T}
 \end{array}
 \begin{array}{l}
 || \tau,^a \\
 \mathbf{0} \\
 \mathbf{1}
 \end{array}
 \begin{array}{l}
 c^{b_{sat}, ;} \\
 -\mathbf{3} \\
 \mathbf{0}
 \end{array}
 \begin{array}{l}
 m^e, || \\
 \mathbf{0} \\
 \mathbf{1} \\
 \mathbf{0}
 \end{array}$$

The undetermined system of variable's exponents is:

$$\begin{array}{rcl} L & & - 3b = 0 \\ M & & b = e \\ T & & a = 0 \end{array}$$

This system doesn't follow the type of solution accepted by the method: integer, positive, minimum and nonzero, two of the exponents, a and b, being equal to zero.

b) The parameters are replaced with others circular permutations and the result we get are two other linear matrixes:

$$\begin{array}{rcl} & || \tau,^a & c^{b_{sat}} ; V^f, || \text{ and} & & || \tau,^a & c^{b_{sat}} ; d^i, || \\ L & 0 & -3 & 3 & L & 0 & -3 & 1 \\ M & 0 & 1 & 1 & M & 0 & 1 & 1 \\ T & 1 & 0 & 0 & T & 1 & 0 & 0 \end{array}$$

Neither one nor the other matrixes follow the type of solution accepted by the method, because a = 0 in both cases.

Commentary: These parameters are not sufficient for describing the process.

The fact that linear dimensions, V and d, are closer to an accepted solutions can be remarked.

c) The process is repeated with the following linear matrixes:

$$|| \tau,^a D^{h_{di}} ; m^e, || \quad || \tau,^a D^{h_{di}} ; V^f, || \quad || \tau,^a D^{h_{di}} ; d^i, ||$$

The solutions are:

$$a = 1; h = 1; e = 0; \quad a = 1; h = 1; f = 2/3; \quad a = 1; h = 1; i = 2;$$

One of the above matrixes generates a solution accepted by the method, containing the diameter of the granule.

The monomial expression is:

$$\tau = k_1 \cdot (d^2/D_{di}), [s] = [s];$$

it is dimensionally homogeneous and can be rewritten as:

$$(\tau \cdot D_{di} / d^2) = k_1 = (Fo_d).$$

Conclusion: The fundamental parameters for the process are: τ , D_{di} , and d, parameters also encountered in the Fourier criteria for diffusion for mass transfer.

d) The simultaneous introduction of the variables that describe the general processes of mass transfer: c_{sat} and D_{di} generate the following linear matrixes:

$$\| \tau,^a c^{b_{\text{sat}}}, D^{h_{\text{di}}}, ; m^e, \| \quad \| \tau,^a c^{b_{\text{sat}}},, D^{h_{\text{di}}}, ; V^f, \|$$

$$\| \tau,^a c^{b_{\text{sat}}}, D^{h_{\text{di}}}, ; d^i, \|$$

None of them contains solutions accepted by the method.

Conclusion: It is very likely for the parameter concentration to have a secondary or reduced importance.

e) Introducing the variable gravitational acceleration, in all the possible permutations, nine in total, does NOT generate solutions accepted by the method.

Conclusion: The parameter gravitational acceleration is a secondary parameter or has a reduced influence on the dissolving process.

f) By introducing the variable dynamic viscosity, in all permutation, nine in total, we do not obtain any solutions accepted by the method.

Conclusion: It is very likely that the parameter dynamic viscosity to have a secondary or reduced importance on the dissolving process.

g) Introducing the kinematic viscosity as a variable, in all possible permutations, nine in total, we obtain only one solution accepted by the method.

	$\ \tau,^a$	$D^{h_{\text{di}}}, ;$	$d^i,$	$v^s \ $
L	0	2	1	2
M	0	0	0	0
T	1	-1	0	-1

The system solution is: $a = 1; s = 1; h = 2; i = 2$, and the monomial expression is:

$$\tau = k_2 \cdot (d^2 \cdot v / D^2_{\text{di}})$$

and can be rewritten as:

$$(\tau \cdot D_{\text{di}}) / d^2 = k_2 \cdot (v / D_{\text{di}}) \quad \text{or} \quad \text{Fo}_d = k_2 \cdot (\text{Sc}).$$

Conclusion: Kinematic viscosity is a secondary parameter or has a very little influence on the dissolving process.

This unic result accepted leads to the idea of verifying the solution's density as a working parameter.

h) By introducing the variable solution's density, in all permutations, nine in total, we obtain a single solution accepted by the method.

	$\ \tau,^a$	$c^{b_{\text{sat}}},$	$D^{h_{\text{di}}}, v^s, ;$	$d^i,$	$\rho^t,$	$\eta^r, \ $
L	0	-3	2 2	1	-3	-1
M	0	1	0 0	0	1	1
T	1	0	-1 -1	0	0	-1

The system's solution is: $a = 1$; $s = 1$; $h = 1$; $i = 2$; $t = 1$; $r = 1$; $b = 2$, and the monomial:

$$\tau = k_3 \cdot (d^2 \cdot \rho \cdot \eta)(c_{sat}^2 \cdot D_{di} \cdot v),$$

or rearranged:

$$\begin{aligned} (\tau \cdot D_{di}/d^2) &= k_3 \cdot (\rho \cdot \eta) \cdot (c_{sat}^2 \cdot \tau) = k_5 \cdot (\rho^2)/(c_{sat}^2); \\ Fo_d &= k_3 \cdot (\rho^2)/(c_{sat}^2). \end{aligned}$$

Conclusion: Obtaining a simplex of similitude, dependent on the solution's density and the concentration at saturation shows that in addition to Fourier's criteria, an essential criteria in the non-steady-state dissolving process, both of the variables can be accounted in some cases, for example when the quantity of solution is considerably higher than the quantity of solid or in the case of reaching the saturation concentration, cases that can not be met when dissolving urea granules in the soil.

i) If the following variables are considered:

	τ, a	c_{sat}, b	D_{di}, h	v, s	;	d, i	m, e	
L	0	-3	2	2		1	0	
M	0	1	0	0		0	1	
T	1	0	-1	-1		0	0	

The system's solutions is: $a = 2$; $s = 1$; $h = 1$; $i = 1$; $t = 1$; $e = 1$; $b = 1$, and the monomial expression is:

$$\begin{aligned} \tau^2 &= k_4 \cdot (d \cdot m)(c_{sat} \cdot D_{di} \cdot v), \quad \text{or rearranged:} \\ (v \cdot D_{di}/d^2)^2 &= k_4 \cdot (D_{di}/v) \cdot (m/c_{sat} \cdot d^3); \\ Fo_d^2 \cdot Sc &= k_4 \cdot (m) \cdot (c_{sat} \cdot d^3); \quad \text{or:} \\ Fo_d^2 \cdot Sc &= k_4 \cdot (C_{particule})/(C_{sat}). \end{aligned}$$

Conclusion: By introducing the variable mass of granule, it was obtained a single solution accepted by the method.

The generation of a new simplex of similitude, dependent on the density of the particle, (which represent the concentration of the solid, m/V , or density of particle, ρ , as well) and the concentration of saturation, shows that in addition to Fourier's criteria, we obtain Schmidt's criteria, Sc , and both variables can be accounted for in some cases, for example when the solid is not pure, or when the concentration at saturation is reached, cases not met when dissolving the granule in soil.

RESULTS AND DISCUSSION

The evolution of dissolving pure and filmed urea granules are presented below:

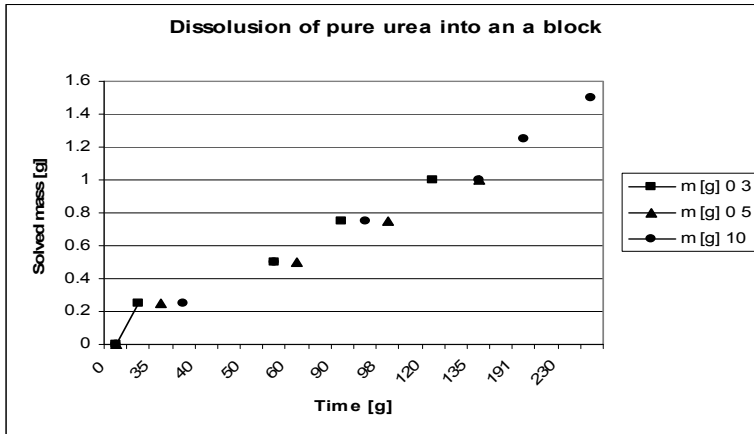


Figure 1. Dissolution of pure urea into block granules

For each determination, the average slope of measures, meaning the average dissolving speed is:

- for 3 [g]; $1/120 = 0.00083$ [g/s];
- for 5 [g]; $1/125 = 0.00080$ [g/s];
- for 10 [g]; $2/326 = 0.00061$ [g/s].

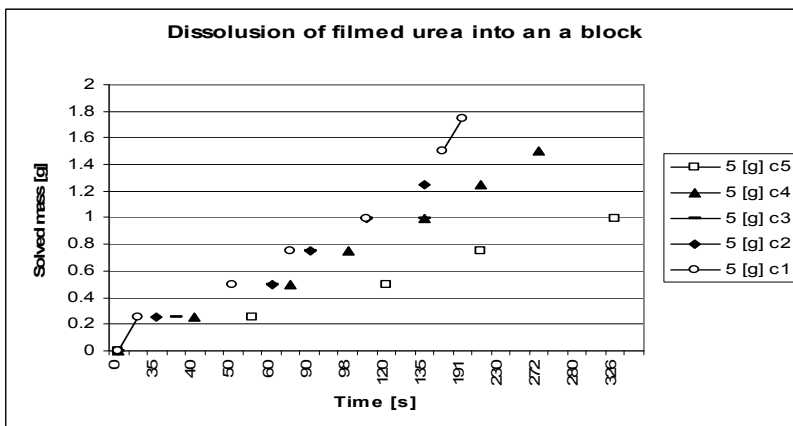


Figure 2. Dissolution of filmed urea into block granules

For each concentration of the varnish, we found values of the dissolving speeds in the following manner:

- c 5) - between 0 and 120 [s]: $0.5/120 = 0.004$ [g/s];
 - between 120 and 326 [s]: $0.5/(326-120) = 0.00243$ [g/s].
- c 4) - between 0 and 75 [s]: $1.0/75 = 0.0066$ [g/s];
 - between 75 and 272 [s]: $0.5/(272 - 75) = 0.005$ [g/s].
- c 3) -between 0 and 60 [s]: $0.5/60 = 0.0083$ [g/s];
 - between 60 and 135 [s]: $0.5/(135 - 60) = 0.0066$ [g/s].
- c 2) - between 0 and 135 [s]: $0.5/75 = 0.0066$ [g/s].
- c 1) - between 0 and 109 [s]: $1.0/109 = 0.0092$ [g/s];
 - between 109 and 162 [s]: $0.5/(162 - 109) = 0.0094$ [g/s];
 - between 162 and 191 [s]: $0.25/(191-162) = 0.0086$ [g/s].

From the graphs and computation results, we noticed a different behavior at dissolving between pure and filmed granules, fact expected to manifest due to the presence of the polymeric film.

The pure granules have a linear and higher dissolving speed than the filmed granules. The film, depending on the concentration of the varnish, meaning the thickness of the film, modifies the behavior of dissolving process.

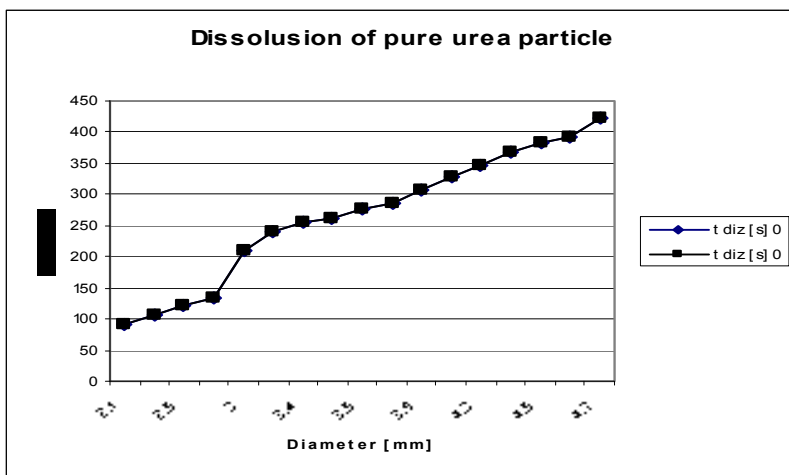


Figure 3. Dissolution of pure urea single particle

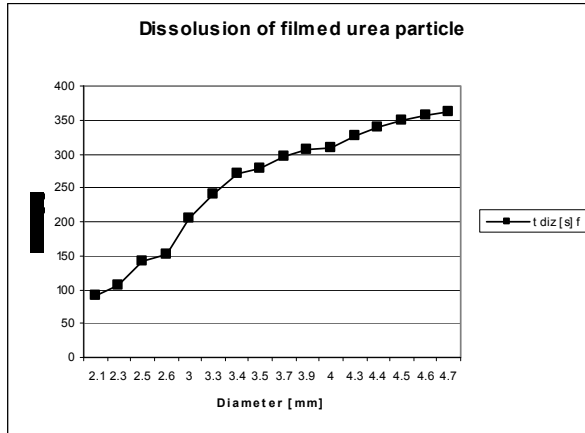


Figure 4. Dissolution of filmed urea single particle

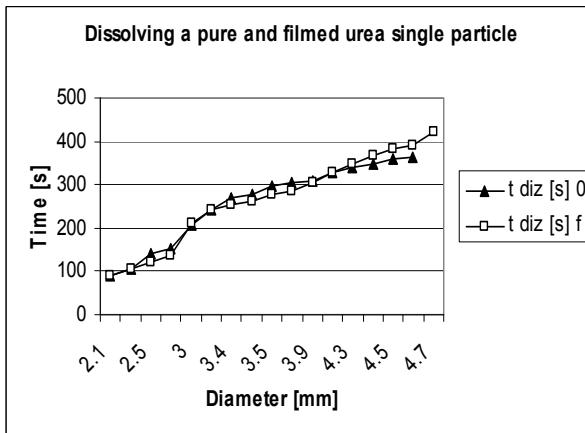


Figure 5. Dissolution of pure and filmed urea single particle

In order to verify the speed determining phase, the classic relations and the relation resulted from the generalized dimensional analysis were tested:

$$(t_1/t_2) = (d_1/d_2)^x, [6];$$

- if $x = 2$ determinant phase is internal diffusion;
- if $x = 1$ determinant phase is dissolution;
- if $x = (1.5 - 2.5)$ determinant phase is external diffusion.

The equation is solved by applying the logarithm:

$$\log(t_1/t_2) = x \cdot \log(d_1/d_2) \quad x = [\log(t_1/t_2)/\log(d_1/d_2)].$$

For pure urea granules the results are presented in Table 1. The values obtained are close to 1, which means that the determining speed step is the dissolution, a fact that is normal and was expected, because the process studied was the dissolution.

Table 1 Dimensional analysis results

Pure urea granules	Filmed urea granules	Ratio	
$x \cdot 2,1/d_i$	$x \cdot 2,1/d_i$	$p \cdot t/d^2$	$f \cdot t/d^2$
0.934479	1.711885	20.45351	20.43084
0.937766	3.472922	19.92439	19.96219
0.941538	1.90115	22.528	19.584
0.74215	2.11096	22.44083	20.0
0.962214	1.665457	22.8	23.35556
0.969388	3.912924	22.08448	22.06612
0.999258	0.931743	23.38235	22.09343
0.947109	1.178802	22.66939	21.72642
1.028271	0.617695	21.65814	22.67755
0.98282	0.397741	20.13807	20.86194
0.958663	0.790347	19.3375	20.13807
1.013165	1.385157	17.71769	20.48125
0.967862	1.360509	17.46901	18.80476
0.97803	1.146694	17.21975	18.9876
1.003171	0.619985	16.89981	18.98272
			19.09914

For filmed urea granules the results are presented in Table 1.

The values presented show a high fluctuation of exponents. If the higher values, at the initial phase of the process, close to '2', show the influence of the polymer film, the external diffusion being the determinant speed phase, in final, the exponent gets close to value '1', so the destroyed film has a smaller influence, and the process gets closer to pure dissolution.

From the generalized dimensional analysis method results that the monomial which describes dissolution, $\tau = k_1 \cdot (d^2/D_{dif})$, can be verified by the experimental data presented above. In order to do so, we formed the ratio: $(\tau/d^2) = k_1 \cdot (1/D_{dif})$, or $(\tau/d^2) = \text{const}$, a plausible fact, considering that the diffusion coefficient is constant at the same temperature. The value of this ratio for pure, (p) and filmed, (f), granules are presented Table 1.

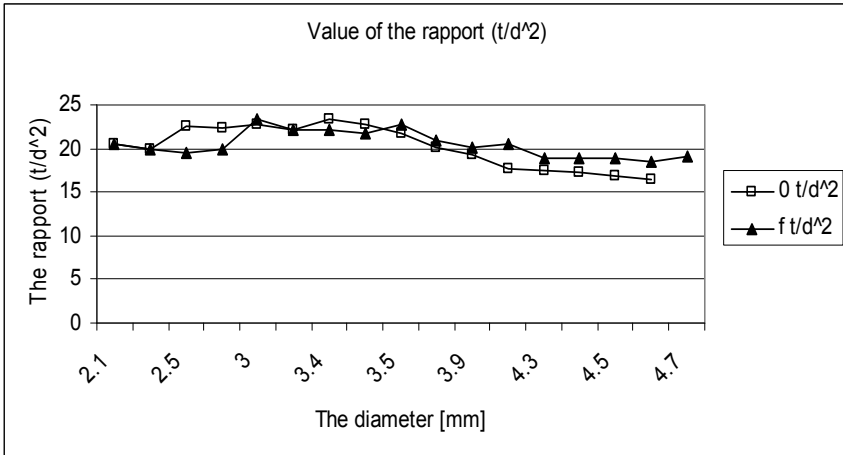


Figure 6. Verifying the monomial constant

In both cases the same effects appear:

- for pure granules, the particle with a diameter between 2.5 and 3.7 [mm] have a different behavior than the rest of diameters studied, 2.1 ÷ 2.3 and respectively 3.9 ÷ 4.7 [mm]. The arrangement of diameters is the same:

2.1 ÷ 2.3 [mm] 2.5 ÷ 3.7 [mm] 3.9 ÷ 4.7 [mm]

- for filmed granules, the evolution is the same, only the diameters differ:

2.1 ÷ 2.6 [mm] 3.0 ÷ 4.0 [mm] 4 ÷ 4.7 [mm].

The nonlinear evolution is in contradiction with the generalized dimensional analysis, where the constant numeric coefficient is stated from the monomial. I put this evolution on the experimental errors, the inaccuracy of measures to both the diameter and the final time of dissolution. Small errors can generate high errors of computation and that is the reason why the values of speed for instantaneous dissolution are not presented here. Getting a relatively narrow interval for the values, 4 units for pure urea, and 8 units for filmed urea, is a reason to continue further measuring of these parameters but in higher accuracy conditions.

CONCLUSIONS

We applied the generalized dimensional analysis method to the dissolving of granules without stirring in liquid.

The main parameters of the process are: the time τ , the diameter of granule d , and the diffusion coefficient D_{dif} .

Kinematic viscosity is a secondary parameter.

The results of the mathematical analysis lead to the following relations:

- the minimum one: $\tau = k_1 \cdot (d^2/D_{\text{dif}})$, or $(\tau \cdot D_{\text{dif}}/d^2) = k_1 = (Fo_d)$.

- the extended one:

$\tau = k_2 \cdot (d^2 \cdot v/D_{\text{dif}}^2)$, $(v \cdot D_{\text{dif}})/d^2 = k_2 \cdot (v/D_{\text{dif}})$ or $Fo_d = k_2 \cdot (Sc)$.

A device for measuring the time of dissolution of a granules quantity was improvised. The speed and the dissolving time depend on the quantity of solid, which is a secondary parameter.

The time or the speed of dissolutions depends on the nature of the solid, pure or filmed. The time increases with the thickness of the film.

The verification of the speed determinant phase for the process lead to a value of 1 for the exponent, meaning that dissolution is the main phase for pure granules and a value close to 2 for filmed granules.

The verification of the numeric coefficient generated by the generalized dimensional analysis method lead to an interval of values higher for the pure solid, 8 units, and a narrower interval for the filmed granules, 4 units.

EXPERIMENTAL SECTION

The objective of the experimental part is the practical determination of pure and filmed urea granule's behavior at dissolution. Filmed urea granules refer to the granules covered in a polymeric compound that generates a thin membrane on the surface of the granule.

For the experimental part of the study of urea without stirring, two sets of experiments were conducted:

1. The dissolution of a set of granules;
2. The dissolution of individual granules.

Materials, tools and methods

- urea granules;
- varnish solutions of various concentrations;
- tap water;
- Berzelius glass, weights, chronometer, calipers.

For the dissolution of a set of granules an experimental device, based on Archimedes's principle was elaborated and applied by the Mohr – Westphal balance. As working principle: the nacelle containing the urea granules is immersed in the glass containing water and then the balance is set to '0'. A determined quantity of granules is then introduced in the nacelle and the balance is set again to the zero value. From this moment, considered '0' as well, the time necessary

to a 0.25 [g] weight to readjust the balance to zero is measured. Then another 0.25 [g] weight is added and the time necessary to readjust the balance is measured. This process is repeated until the granules are completely dissolved and the balance becomes immobile.

The filming of the granules was performed by immersing the granules into a varnish with different concentrations, draining the excess varnish and drying the granules through continuous stirring in the vase, at atmospheric conditions, until complete drying. The stirring was performed through continuously rotating the recipient in order to avoid the granules to stick to each other during drying.

The varnish concentration was determined in the following manner:

- a quantity of varnish of 38.4 [g] was left in a capsule until reaching a constant mass. The quantity of solid resulted was 0.82 [g]. The initial concentration of the varnish is 2.135 [%].

- the solution was gradually diluted to double, resulting the following working concentrations:

5) 2.135 [%]; 4) 1.068 [%]; 3) 0.534 [%];
2) 0.267 [%]; 1) 0.133 [%].

- for each determination 500 [ml] of water were used, in order to get closer to an infinite dilution, but mostly for providing enough space for the nacelle to travel vertically during the determination.

- quantities of 3, 5, and 10 [g] of pure granules and 5 [g] of filmed granules were used.

- the working temperature was room temperature, 20 [°C].

For the dissolutions of individual granules, the method was simple: the diameter of granule was measured, then the time it passed from the moment of immersing it in 500 [ml] of water and it's visual desperation.

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