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AN ACOUSTIC METHOD FOR THE DETERMINATION OF DISPERSIVECOMPOSITION OF ORGANIC SUSPENSIONS

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In this paper it is shown that the sedimentation analysis of an organic suspension can be made rapidly using ultrasonic methods in which an ultrasonic plane wave is used to induce very rapid sedimentation of the dispersed phase, while a transversal ultrasonic wave is used to determine the course of the changing concentration of the dispersed phase during sedimentation in the ultrasonic field. A description of the measuring system as well as results of experimental studies for determining the dispersive composition of some organic suspensions are given.

1. Introduction

A knowledge of the dispersive composition of organic suspensions is especially important during the inspection of technological processes. The methods used hitherto in industry for the investigation of the dispersive composition of these systems are very time-consuming [4, 5, 6], and for this reason are not suitable for the control of technological processes.

Thus, the problem arises of finding a rapid measurement method, i.e. a method which would give virtually instantaneously information on the conditions in the dispersive system as they change with time.

In this paper we show that the instantaneous condition of a dispersive system can be determined with the aid of an acoustic method by measuring the wave impedance of the tested dispersive system during the "settling" of molecules of the dispersed phase in an ultrasonic field.

2. "Settling" of molecules of the dispersed phase in the field of a plane acoustic wave

In initially considering the influence of an acoustic plane wave on the distribution of the concentration of molecules suspended in a dispersive system we shall assume the following:

(a) the molecules of the dispersed substance have spherical symmetry, with the molecule radius considerably smaller than the wavelength of the ultrasonic plane wave;

(b) the radii and masess of molecules of the dispersed phase and the dispersing substance satisfy the relations $r \gg r_0$ and $m \gg m_0$;

(c) the medium is considered to be lossless so that instantaneous velocities result only from the same wave conditions.

On the basis of these assumptions we can apply KING's [7] theory for solving the problem concerning the action of the acoustic radiation pressure on a sphere. According to this theory, in a sound wave propagating within the system a suspended spherical molecule is acted upon by the force. In the case of the plane wave this force is expressed by the formula

$$F = \pi g_0 |A|^2 \sin(2kx) \left\{ \frac{1}{aT_0T_1} - \frac{2[a^2-3(1-\varrho_0/\varrho_1)]}{a^5T_1T_2} + \right.$$
$$\left. + \frac{3(a^2-8)}{a^7T_2T_3} - \dots \right\}, \tag{1}$$

where

$$a = kr, \quad k = \frac{2\pi}{\lambda}, \quad T_0 = a^{-1}, \quad T_1 = \frac{2+\varrho_0/\varrho_1}{a^3},$$

$$T_2 = 9a^{-5}, \quad T_3 = 60a^{-7}, \quad \dots, \quad T_n = \frac{1\cdot 3 \dots (2n-1)(n+1)}{a^{2n+1}},$$

r denotes the molecular radius of the dispersed phase.

From expression (1) we obtain an approximate formula in the form

$$F = \pi g_0 |A|^2 \sin(2kx)\, a^3 \frac{1+\frac{2}{3}(1-g_0/g_1)}{2+g_0/g_1} + R(a^i), \quad i = 4, 5, \dots, \tag{1a}$$

where $R(a^i)$ denotes the remaining terms of a series containing the terms $z(a^4)$ and higher.

With the assumption that the molecular radius of the dispersed phase is considerably smaller than the ultrasonic wavelength ($a \ll 1$), it is possible to neglect the terms $z(a^4)$ and higher in formula (1a), whence we obtain

$$F = \pi g_0 |A|^2 \sin(2kx)\, a^3 \frac{1+\frac{2}{3}(1-g_0/g_1)}{2+g_0/g_1}, \tag{2}$$

where g_0 and g_1 denote the density of the dispersing and dispersed media, respectively.

As can be seen from formula (2), this force is equal to zero for the nodes and antinodes of the vibrations and attains its maximum between them. It can be easily proved that the direction of this force depends on the value of relative density g_0/g_1 of the dispersed substance. Thus, for example, with a relative density of the molecules of the dispersed phase $g_0/g_1 < 2.5$, this force is directed towards the antinodes, whereas with a relative density of the molecules of $g_0/g_1 > 2.5$ it will be directed towards the nodes of vibration. This means that under the action of the wave pressure the molecules suspended in the medium will move – depending on the value of g_0/g_1 – towards the antinodes or nodes of vibration. Thus in the presence of a stationary plane wave in a dispersive system there is a change in the concentration distribution of the molecules of the dispersed phase. These conclusions have been confirmed by numerous experiments [3, 6, 7].

The phenomenon described above constitutes an analogue of gravitational sedimentation and therefore will in future be called *acoustic sedimentation*.

Let us first consider the process of acoustic sedimentation in a monodispersive system. Let us assume that the molecules suspended in the system move only under the action of the acoustic field, i.e. the dispersing medium is sufficiently viscous and the size of molecules of the dispersed phase sufficiently large. It is then possible to neglect the thermal and gravitational motion of these molecules. The equation of motion for one molecule suspended in the medium takes the form

$$6\pi\eta r\frac{dx}{dt} = \pi g_0|A|^2(kr)^3\sin(2kx)\,\frac{(5g_1-2g_0)}{(6g_1+3g_0)}, \tag{3}$$

where η denotes the viscosity of the dispersing medium, r – the molecular radius of the dispersed phase, $|A|$ – the amplitude of the acoustic potential, g_0 and g_1 – the densities of the dispersing and dispersed media, and x – the distance of a suspended molecule from the plane of an antinode.

Integrating this equation, we obtain

$$\tan(kx) = \tan(kx_0)\,e^{Bt}, \tag{4}$$

where

$$B = \frac{8\pi^2 r^2 \bar{E}(5g_1-2g_0)}{3\lambda^2\eta(6g_1+3g_0)},$$

and $\bar{E}$ denotes the acoustic energy density.

Let us further assume that the suspended molecules do not interact (λ is constant during the acoustic sedimentation) and initially are evenly distributed within the whole of the distributing system, so that the number of molecules suspended between planes x_0 and x_0+dx_0 is $n_0\,dx_0$, where n_0 denotes the concentration of molecules at $t = 0$. Then after a time t of the acoustic sedimentation the number of suspended molecules, contained between planes x and $x+dx$, is $n\,dx$, where n denotes the concentration of molecules after a time t of the process.

Under these conditions we have

$$n\,dx = n_0\,dx_0. \tag{5}$$

According to equation (5) we find from formula (4) that the distribution of relative concentration (n/n_0) is given by the expression

$$\frac{n}{n_0} = (\cosh Bt - \cos(2\,kx)\sinh Bt)^{-1}. \tag{6}$$

Figure 1 shows the distribution of relative concentration of suspended molecules which hase been calculated for the case of a suspension consisting of dispersed particles of radius 1 μm, viscosity $\eta = 18.5$ cP, in an ultrasonic field of frequency 20 kHz and energy density 10^{-4} J/cm³, at $t_1 = 210$ s and $t_2 = 430$ s.

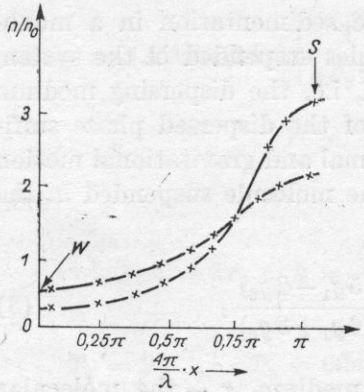

Fig. 1. Distribution of molecular concentration of the dispersed phase evaluated at times $t_1 = 210$ s and $t_2 =$ $= 430$ s during acoustic sedimentation

W and S denote the corresponding positions of a node and an antinode vibration

The curves plotted in Fig. 1 for an ideal suspension show that at a small intensity of the ultrasonic field (about 2 W/cm²) the molecules of the dispersed phase concentrate under the action of the wave pressure at the antinodes of the stationary ultrasonic wave. Substituting particular values into formula (6) it can be shown that in a plane x the concentration of molecules of the dispersed phase at the nodes decreases, but at the antinodes it increases exponentially with the duration of the acoustic sedimentation

$$n_w = n_0 e^{-Bt}, \tag{7a}$$

$$n_s = n_0 e^{Bt}, \tag{7b}$$

where n_w and n_s denote the concentrations of the molecules of the dispersed phase at the nodes and at the antinodes after a time t of the duration of the process.

From formulae (7a) and (7b) we obtain

$$n_w n_s = n_0^2. \tag{8}$$

This relation constitutes the characteristics of a dispersive system in which the sedimentation occurs under the influence of an ultrasonic field of plane stationary waves.

Let us now consider the process of acoustic sedimentation of molecules in a polydispersive suspension consisting of a certain number of different sizes of molecules of dispersed phase.

Using formula (6) and the assumption that the density of the dispersed molecules does not depend on their radius, the distribution of the volume concentration of the dispersed molecules in a polydispersive medium during acoustic sedimentation takes the form

$$\varphi_{x,t} = \sum \varphi_{0,i}\left(\cosh B_i t - \cos(2kx)\sinh B_i t\right)^{-1}, \tag{9}$$

where $\varphi_{x,t}$ denotes the volume concentration of dispersed molecules in the plane x at a time t, $\varphi_{0,i}$ is the volume concentration of the dispersed molecules of the i-th size at time $t = 0$, and

$$B_i = \frac{8\pi^2 \bar{E}(5g_1 - 2g_0)}{3\lambda^2 \eta(6g_1 + 3g_0)} r_i,$$

where r_i denotes the radius of a suspended molecule of the i-th size and $\bar{E}$ – the acoustic energy density.

From formula (9) it can be seen that the volume concentration of the dispersed molecules in a polydispersive suspension – as in the case of monodispersive system – decreases at the nodes of vibration, while at the antinodes it increases exponentially during the acoustic sedimentation process.

3. Analysis of acoustic sedimentation

When an organic suspension is polydispersive, the molecules of the individual fractions sediment under the influence of the field of plane stationary waves at different rates. Let us assume that the volume of molecules of the dispersed phase consists of volume fractions $\varphi_1, \varphi_2, \ldots$ corresponding to the radii $r_1, r_2, \ldots$ Then we can write

$$\varphi = \sum \varphi_i.$$

From formula (9), a change in the volume concentration caused by molecules wholly leaving the area, e.g. at a node of vibration, is

$$\Delta\varphi_{w,t} = \sum \varphi_{0,i}(1 - e^{-B_i T}), \tag{9a}$$

where $\varphi_{0,i}$ denotes the volume concentration of dispersed molecules of the i-th size at $t = 0$.

The change of volume concentration $\Delta\varphi_{w,t}$, brought about during the acoustic sedimentation, is determined by an ultrasonic transversal wave resonator [10, 11].

Using:

(a) the expression for the wave impedance of a medium

$$Z_L = R_L + iX_L, \tag{10}$$

(b) the relation between the viscous and elastic components of the wave impedance at a frequency $\omega \ll \omega_r$ [8]

$$R_L = X_L = (\pi f \eta_s g)^{1/2}, \tag{11}$$

(c) Einstein's law for the viscosity of a suspension

$$\eta_s = \eta_0(1 + b\varphi_{x,t}), \tag{12}$$

(d) the relation between the attenuation coefficient of an ultrasonic resonator and the wave impedance of the medium [9]

$$a = k_0 Z_L, \tag{13}$$

we can derive a relationship between the volume fraction of dispersed molecules and the attenuation coefficient of the resonator in the form

$$a_t^2 = a_0^2(1 + b\varphi_{x,t}), \tag{14}$$

where a_t and a_0 denote the attenuation coefficients of the dispersive system and the dispersing substance, while $\varphi_{x,t}$ is the volume fraction of the dispersed molecules.

Hence, by measuring the attenuation coefficient of an ultrasonic resonator it is possible to determine experimentally the time dependence of the volume concentration of dispersed molecules in a particular region, e.g. at a node of vibration during acoustic sedimentation.

From expression (14) it is possible to change the volume concentration of dispersed molecules. In the region of a node of vibration it takes the form

$$\Delta\varphi_{w,t} = \overline{\Delta} a_{w,t} b^{-1}, \tag{15}$$

where

$$\overline{\Delta} a_{w,t} = \frac{a_0^2 - a_{w,t}^2}{a_0^2}$$

denotes the change of the relative attenuation coefficient of the vibrations caused by a change in the volume concentration of the dispersed molecules due to some leaving the region of the node of vibration.

If we give further consideration to the fact that B_i is generally of the order of 10^{-4} and use expressions (9) and (15), it can be easily proved that the basic equation of acoustic sedimentation can be written in the following manner:

$$\overline{\varDelta a}_{w,t} = \overline{\varDelta a}_{w,r} + \overline{\varDelta a}_{w,2} = \overline{\varDelta a}_{w,r} + t\,\frac{d(\overline{\varDelta a}_{w,t})}{dt}. \tag{16}$$

It consists of the following components:

(a) changes of relative attenuation coefficient $\overline{\varDelta a}_{w,r}$, contributed by the fraction of molecules with a radius larger than a certain value, which could leave wholly the region of the node of vibration, expressed in terms of the initial concentration of these fractions, and

(b) changes of relative attenuation coefficient $\overline{\varDelta a}_{w,2}$ caused by the part of the molecular fractions with a radius smaller than the limiting value of the radius, which have left the volume under consideration.

This change is in the form of the product of the instantaneous derivative of the change of the relative attenuation coefficient caused by the acoustic sedimentation of all the molecules at a time t and the duration of this process up to the time t.

This equation is completely analogous to the expression representing the settlement curve in the analysis of gravitational sedimentation. Thus, in the analysis of acoustic sedimentation we can proceed further as in the gravitational sedimentation analysis to the transition from a settlement curve to a distribution curve. In order to determine the molecular distribution curve of the dispersed phase as a function of the radius, we evaluate the ratio $d(\overline{\varDelta a}_{w,r})/dt$ for the molecules, which have left the region of the node of vibration

$$\frac{d(\overline{\varDelta a}_{w,r})}{dr} = \frac{d(\overline{\varDelta a}_{w,r})/dt}{dr/dt}. \tag{17}$$

The value of the ratio dr/dt can be found from the expression for the "settlement" time of all molecules of radius r or greater,

$$t = \frac{L}{r^2}, \tag{18}$$

where

$$L = \frac{3\times 10^5 \lambda^2 \eta (6g_1 + 3g_0)}{8\pi^2 \bar{E}(5g_1 - 2g_0)}. \tag{19}$$

Using expression (18), we obtain

$$\frac{dr}{dt} = -\frac{1}{2}\sqrt{\frac{L}{t^3}} = -\frac{r}{2t}. \tag{20}$$

Substituting into equation (17) the values for $d(\overline{\varDelta a}_{w,r})/dt$ and dr/dt, we have

$$\frac{d(\overline{\varDelta a}_{w,r})}{dr} = \frac{2t^2}{r}\,\frac{d^2(\overline{\varDelta a}_{w,t})}{dt^2}. \tag{21}$$

This equation expresses the separation of the molecules according to their size.

Figure 2 shows the dependence of $\overline{\Delta a}_{w,t}$ on time, obtained experimentally. When we draw the tangent to the curve at the point which corresponds to the time of acoustic sedimentation t, it will intersect the ordinate axis at a certain value s which is equal to the change of the relative attenuation coefficient of the resonator $\overline{\Delta a}_{w,r}$ caused by the change of volume concentration of molecules with radius r and larger, which have left the region of the node of vibration after a time t, i.e.

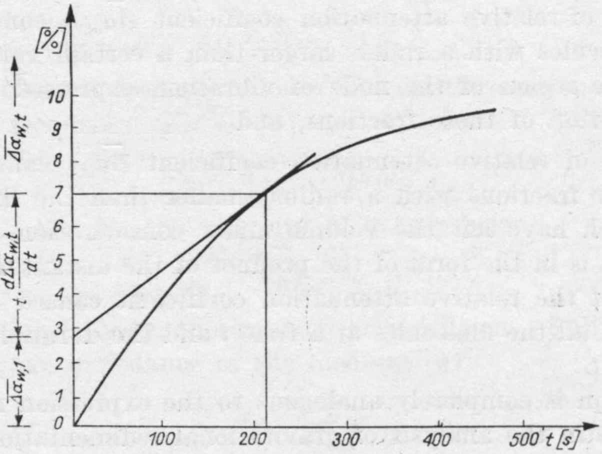

Fig. 2. "Settlement" curve of molecules of the dispersed phase at a node of vibration during acoustic sedimentation

$$s = \overline{\Delta a}_{w,r} = \overline{\Delta a}_{w,t} - t\,\frac{d(\overline{\Delta a}_{w,t})}{dt}.$$

Drawing a number of tangents to the curve at points corresponding to equal lengths of time, we can determine on the ordinate axis the differences in the lengths $\Delta(\overline{\Delta a}_{w,t})$. Since, however,

$$\frac{ds}{dr} = \frac{d(\overline{\Delta a}_{w,r})}{dr},$$

we can find, knowing $\Delta(\overline{\Delta a}_{w,r})$, the value of Δr. Thus, plotting r as the abscissa, we obtain the curve of molecular separation $[\Delta(\overline{\Delta a}_{w,r})/\Delta r]$.

4. Measuring system

Experimental investigations of acoustic sedimentation were performed with the measuring system shown in the block diagram in Fig. 3. The ultrasonic sedimentator consists of a source of ultrasonic plane waves, an electronic

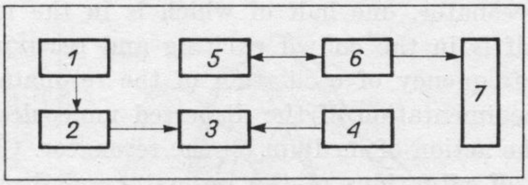

Fig. 3. Block diagram of the system for the measurement of acoustic sedimentation of the dispersed phase

1 – electric generator, *2* – magnetostrictive transducer with acoustic transformer, *3* – measurement vessel, *4* – ultrasonic wave reflector, *5* – sensor of measurement of the wave impedance of the tested system, *6* – system of excitation and reception of vibration, *7* – electronic system for the digital recording of measurement results

device for measurement of wave impedance of the suspension, an electronic system for digital recording, a thermostat and a measurement vessel with relatively rigid walls which effectively prevents the tested suspension from vibrating radially.

The ultrasonic generator is an electrical system with magnetostrictive transducer. The maximum power of the generator is 400 W and the transducer frequency is 20 kHz. The measurement vessel is formed as a brass cylinder of diameter 4 cm and height 10 cm. Over the measurement vessel there is the ultrasonic transducer with an acoustic transformer. Brass has been used for the construction of acoustic transformer. The lower part of the measurement vessel is a cylindrical reflector, its height corresponding to 5/4 of the ultrasonic wavelength in brass. The tranducer together with the acoustic transformer over the vessel can be shifted continuously by means of a screw. The cross-section of the measurement vessel is shown in Fig. 4. Vertically to the direction

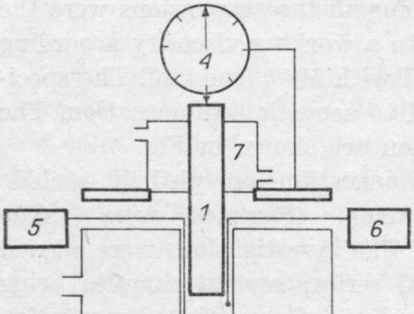

Fig. 4. Cross-section of measurement vessel of the acoustic sedimenter

1 – reflector, *2* – acoustic transformer, *3* – ultrasonic generator, *4* – sensor for measurement of the distance of the reflector from the source of the ultrasonic waves, *5* – thermistor thermometer, *6* – system for measurement of the wave impedance of the tested suspension, *7* – thermostat of movement of the ultrasonic transversal wave there is placed the ultrasonic transversal wave resonator, one half of which is in the measurement vessel, while the other half is in the coil of exciting and receiving vibrations [11]. The characteristic frequency of oscillation of the resonator is 30 kHz.

The acoustic sedimentation of the dispersed molecules in the tested suspensions changes the action of medium on the resonator. Changes in the value of the attenuation of vibrations of the resonator are directly recorded by a digital printer.

5. Experimental procedure

In order to check the results of sections 2 and 3, investigation of dispersive composition using the above method were carried out on 2-component and polycomponent suspensions. The choice of the components and composition of the simple suspensions was decided by the composition and kind of the multicomponent organic suspensions to be tested.

Firstly, an analysis of acoustic sedimentation on 2-component suspensions with the following composition (designations of the composition according to standard PN – MPCH – 07) was made:

1 – suspension No 1 – 10%: 45/60% + titanium white,
2 – suspension No 2 – 10%: 45/60% + iron oxide red,
3 – suspension No 3 – 10%: 45/60% + poliogengelb RT 1560,
4 – suspension No 4 – 10%: 45/60% + monostral jast blue RFS.

These suspensions were prepared according to the following method: the pigment (in the ratio 1 : 1) has been mixed with resin mechanically and then ground in a disc mill. The grinding conditions for all the suspensions were the same. The suspensions obtained were thinned to a working viscosity according to Ford cup for 30 s in a solution melolak B/II with 50% budanol. The specimens, prepared in this manner, were subjected to acoustic sedimentation. The results of the analysis of acoustic sedimentation are shown in Fig. 5.

Secondly, the analysis of acoustic sedimentation on phthalic-carbide enamel (Manuf. No 3463-312-360) was made. (Samples were taken directly from the Paints and Lacquer Factory. The investigations were carried out on samples taken from various industrial series; several samples being prepared from each series. The results of the analysis of acoustic sedimentation of these samples are shown in Fig. 6.

The duration of the acoustic sedimentation for the single samples did not exceed 8 minutes. When a digital computer was used to analyse the obtained results, the time of the analysis of the acoustic sedimentation was equal to the duration of the process of acoustic sedimentation of the molecules dispersed in the suspension.

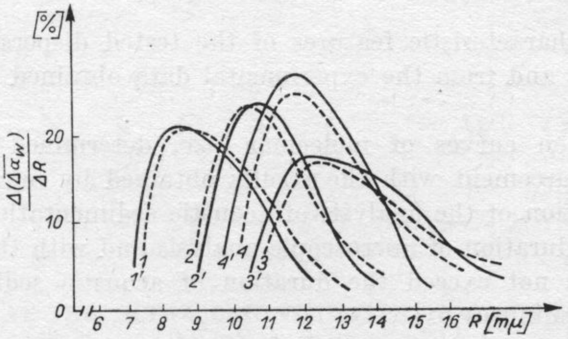

Fig. 5. Distribution of pigment molecules in suspensions *1, 2, 3, 4* according to their radius determined: a) by the acoustic method *1, 2, 3, 4*, b) by microscopy *1′, 2′, 3′, 4′*, with confidence limits for the determination of r of $\Delta r = \pm 0.5$ μm

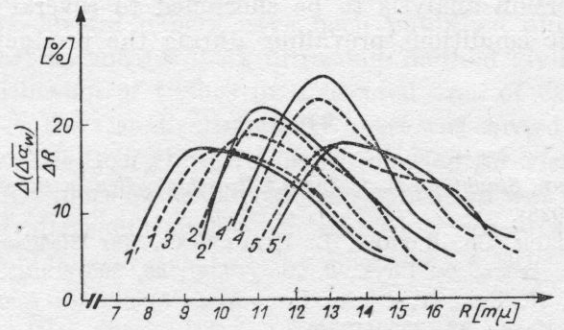

Fig. 6. Distribution of pigment molecules in enamel series *1, 2, 3, 4, 5* according to their size, determined by: a) the acoustic method *1, 2, 3, 4, 5* and b) microscopy *1′, 2′, 3′, 4′, 5′*, with confidence limits for the determination of r of $\Delta r = \pm 0.5$ μm

For some suspension additional investigations of dispersive composition were made by a microscopic method [5]. The preparation grain counting and the calculation of real value of grain distribution were performed according to the recommendations of the standard PN-70/C-04424. The results of investigations are shown in Figs. 5 and 6.

It follows from the results of the measurements presented in Figs. 5 and 6 that the distribution curves of molecule size, determined by the acoustic method, are in agreement with those obtained by microscopy.

6. Conclusions

On the basis of the experimental results obtained, it can be said that the above analysis and the conclusions resulting from it conveys a picture of the process of acoustic sedimentation, with the aid of which it is possible to describe the characteristic features of the tested dispersive system. Thus from the analysis and from the experimental data obtained the following can be concluded:

(a) distribution curves of molecular size, determined by the acoustic method, are in agreement with the results obtained by microscopy;

(b) the duration of the analysis of acoustic sedimentation is considerably shorter than the duration of microscopic analysis and with the use of a digital computer it does not exceed the duration of acoustic sedimentation which lasts only a few minutes;

(c) it can be said, moreover, that the dispersive compositions of enamel samples from various industrial series are different.

From the above it can be seen that the acoustic method, described for the determination of the dispersive composition of organic suspensions, can be used during the inspection of technological processes, since it permits the time of the dispersion analysis to be shortened to several minutes and this corresponds to the conditions prevailing during the production.

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