

# Determination of the Density Dispersion of Suspension Poly(vinyl Chloride) by the Method of Kinetic Density Curves

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## Synopsis

A new method has been developed for the evaluation and comparison of quality of various types of poly(vinyl chloride) (PVC) powder with respect to their density homogeneity. The method consists in the determination of the dependence of the volume of a specifically heavier fraction of PVC powder on the density or concentration of testing aqueous  $\text{NaNO}_3$  solutions after a chosen time of contact between the powder and the testing solutions. Compared with the method of determination of density distribution using densitometric titration, the new method simplifies and extends possibilities of comparison of polymers and improves the density characterization.

## INTRODUCTION

The density of solid compounds can be determined using a number of standard methods<sup>1</sup> which provide average density values: For compact compounds upward pressure is measured; pycnometric methods are used for small and irregular pieces; porous material are measured by means of a helium densitometer. The suspension method, by which the density even of a single particle can be determined, holds a special position; such a particle can also be distinguished in the given assembly from those specifically lighter, which sediment at the surface of the liquid, and from those of higher density, which accumulate at the bottom. The suspension principle is used in the density determination in a density gradient. Also, the method may be employed in an evaluation of the density homogeneity of a large body, if the latter can be disintegrated without interference with the morphological structure; the chips or particles thus obtained may be investigated by the suspension method.

The density distribution of PVC powders is one of the criteria of homogeneity, which considerably affect the processing properties of mixtures prepared from them, and particularly of the final parameters of transparent products. The suspension PVC powders usually contain opaque porous particles, 10–300  $\mu\text{m}$  in size. In addition to normal particles, the powders also contain particles which are difficult to process; these are usually nonporous, glassy, and compact.<sup>2</sup> The occurrence of such particles gives rise to problems both for the manufacturer and for those involved in their processing, because the presence of the particles reveals itself only additionally, after processing to products.

Difficult processible particles are determined by employing a standard method<sup>3</sup> in which a thin foil is used, made from a mixture of the dry PVC

powder, carbon black, plasticizer, and additives, using calandering and press molding under standard conditions; the unprocessable particles are detected on the black foil by observing the number of light or translucent points—"fish eyes." The result is given in the number of fish eyes per 1 g tested PVC. The disadvantage of the standard method is, however, that the difficult-processible particles with a diameter smaller than the thickness of the testing foil are usually neither determined nor detected by employing this procedure. At the same time, they are the basic obstacle in the case of highly demanding applications, such as transparent products, and particularly optical elements and auxiliary pieces.

The problem of homogeneity of PVC powders has been dealt with in many papers. Balakirskaya and Shtarkman<sup>4</sup> fractionated powders of suspension PVC for a morphological investigation by means of methanol-tetrachloromethane mixtures of various density. Defife<sup>5</sup> also used this method as one of the characterization techniques of evaluation of the PVC powders and their suitability for a certain type of processing. In addition to the procedure just mentioned,<sup>4</sup> Defife<sup>5</sup> also reports a microscopic method, consisting of the observation of uniformity of the gradual penetration of silicone oil into the PVC particles. Homogeneity is evaluated on the basis of the time dependence of the optically transparent and opaque fractions of PVC grains exposed to the effects of silicone oil. In Ref. 5, the microscopic method of observation of the penetration of solvent and of the decomposition of grains into primary particles caused by quinoline according to Tregan<sup>6</sup> is also reported, and its use is described.

Horáček and Pánková<sup>7</sup> showed that by adding dioctyl phthalate ( $\rho = 0.9 \text{ g cm}^{-3}$ ) to the PVC powder ( $\rho = 1.4 \text{ g cm}^{-3}$ ) at  $80^\circ\text{C}$  in a Brabender mixer, a mixture of partly swollen particles is obtained, which can be fractionated by using  $\text{ZnSO}_4$  solutions of various density, thus giving fractions enriched in "fish eyes." They experimentally checked an assumption that easily processible particles will preferentially interact with the plasticizer, thus reducing their density, while difficult-processible particles interact less readily. Specifically heavier fractions were separated by centrifugation, and then washed and weighed. By plotting the dependences of weight fractions of isolated heavier fractions on the density of  $\text{ZnSO}_4$  solutions, density distribution curves were obtained for the given type of PVC powder. The position of these curves depended on the weight ratio of the plasticizer and of the original PVC. The fraction of the highest density contained the highest amount of fish eyes. According to the authors, a shortcoming of the method is the necessity to use a dry mixture: during its preparation, the plasticizer at elevated temperature attacks the structure of almost all particles, thus reducing the possibility of a further morphological investigation of separated fractions.

Lukáš et al.<sup>2</sup> obtained glassy compact particles from samples of suspension PVC, which according to a standard test contained a large amount of fish eyes, by manual sorting under an optical microscope, and proved that these particles were difficult-processible ones, which coincide in their molecular parameters with normal particles, but differ in morphology.

Lukáš et al.<sup>8</sup> found that in a suspension of polymerizing vinyl chloride, in the case of a nonuniform distribution of the initiator (especially if major drops of initiator are formed), an increased formation of difficultly processible particles takes place. According to the authors, the formations of these

particles is probably related to a polymerization mechanism different from the polymerization in normal particles. The lower heat stability of difficult processible particles is a consequence of a side reaction between the initiator and PVC chains. Already under the polymerization conditions dehydrochlorination and formation of internal double bonds in PVC chains occurs. The difficult processibility of glassy particles was explained by the water content retained in their bulk due to their compact morphological structure. During processing, water present inside the particle impedes an efficient interaction between PVC and the plasticizer.

In our previous paper,<sup>9</sup> we described a nondestructive separation of suspension PVC powders or their sieve fractions by using  $\text{NaNO}_3$  solutions of various density. The densitometric titration, which is the term used by us for the separation and characterization procedure, is a dynamic (i.e., dependent on the history of the sample) method which describes the density dispersion of the sample and makes possible a mutual comparison between e.g., the individual production charges; the sample can also be compared with a standard, which is known to be suitable for the intended application.

This paper reports a new method, which unlike the densitometric titration, provides wider possibilities of the characterization and comparison of polymers.

## EXPERIMENTAL

### Polymers

Commercial suspension poly(vinyl chloride) powder Neralit S 652 and Neralit S 702 (Spolana Neratovice, Czechoslovakia) and an archive sample of Neralit S 702 FE containing 36 fish eyes (FE)/g PVC were used. A detailed granulometric analysis and other data were reported in a previous paper.<sup>9</sup>

### $\text{NaNO}_3$ Solutions

The basic solution was prepared by dissolving 400.00 g  $\text{NaNO}_3$  AR grade, dried to constant weight, in 600.00 g of degassed distilled water. Solutions having other concentrations were prepared by adding a calculated quantity of water to the weighed quantity of the basic solution.

### Dependences of the Volume of a Specifically Heavier PVC Phase on Time

To weighed (1.00 g) amounts of the fraction of dry PVC powder in calibrated centrifugal test tubes (total volume 6.5 mL), 3.5 mL of solutions of chosen  $\text{NaNO}_3$  concentrations were added. The test tubes were closed with PE stoppers and fixed perpendicularly to the axis in an inclined rotating holder, and their content was stirred by slow (4 rpm) rotation of the holder in a water thermostat (298.16 K). After a fixed time the test tubes were centrifuged (centrifuge "Chirota," 5 min, 60 G at the surface level), and volumes of the specifically heavier PVC phases were read off. The procedure was repeated until a constant volume of the specifically heavier PVC phase was reached. Kinetic density curves were obtained by plotting volumes of the specifically heavier PVC phase (at a chosen time of contact between the sample and the

testing solutions) against the concentration of the  $\text{NaNO}_3$  solution (i.e., implicitly against density).

## RESULTS AND DISCUSSION

In our previous paper<sup>9</sup> we described the determination of density distribution by employing the densitometric titration method. The procedure consisted in that the dependence of the volume of the specifically heavier PVC fraction on the concentration of  $\text{NaNO}_3$  was determined using a standard weighted amount (1.00 g) of the sieve fraction of PVC powder suspended in an  $\text{NaNO}_3$  solution. The concentrations of  $\text{NaNO}_3$  were reduced during the determination by gradually adding water to the mixture from the original 40%  $\text{NaNO}_3$  to the required dilution. We showed that during the determination itself due to the porosity of PVC grains a number of transport processes was operative:

1. Penetration of the concentrated  $\text{NaNO}_3$  solution into grain pores, which gradually raised the average density of the individual PVC particles.
2. Dissolution of air from pores in the penetrating solution, which enabled more liquid to enter the pores.
3. Diffusion of dissolved air from the particles.

After the required amount of water had been added, the testing solution outside the particles became immediately diluted, while the establishment of equilibrium in pores was a function of time, due to:

4. Diffusion of water into more concentrated solution in pores.
5. Countercurrent diffusion of  $\text{NaNO}_3$  into the external solution.
6. Increased velocity of air transport from pores caused by the decreasing concentration of  $\text{NaNO}_3$ , and hence to the increasing solubility of air in the solution in pores.

Processes 1–6 occurring in parallel are the reason why the densitometric titration method is a dynamic method, i.e., it depends on the sample history, and explains why reproducible results could be reached only by observing a procedure once selected. In the case of titration, a number of points could be selected to characterize the density distribution, but this number is compulsory for subsequent determinations and cannot be varied without committing serious errors. If the number of points is low—even though these points are adequately distributed on the S-shaped part of the distribution curve—there is still the risk that another type of PVC which differs from the first sample in its dynamic density parameters will be characterized insufficiently, because most points will lie beyond the characteristic region. On the contrary, the large number of points within a broad density (i.e., concentration) range of  $\text{NaNO}_3$  solution inadequately raises the laboriousness and requirements to exactness of the whole procedure. If there were any error or deviation during the titration, it was not possible to prepare a new sample, and thus to continue the preceding stage of determination. The whole titration had to be repeated starting from the very beginning; otherwise the dependence on the

sample history was reflected in an instantaneous discontinuity on the density distribution and in a different slope of the dependence. For these reasons, the densitometric titration is particularly suited for a comparison between the individual charges of the same type of PVC, where the determination by using 3–5  $\text{NaNO}_3$  concentration is sufficient to characterize the distribution. Then the advantages of densitometric titration become fully operative—namely, its rate and the low consumption of the sample, because the whole determination of density distribution can be performed using a single weighed quantity.

Shortcomings of the densitometric titration are removed by employing the method described in the Experimental section. The new procedure allows us to choose an arbitrary and mutually independent number of determination of points lying on the kinetic or equilibrium dependences of volumes of the specifically heavier PVC phase on the concentrations of  $\text{NaNO}_3$  solutions with which the standard weighed quantities (1.00 g) are in contact for the chosen time. The method is again a dynamic one, but, in view of its basis described above for the densitometric titration, only transport phenomena 1–3 are operative in this case. Typical time dependences of volumes of the specifically heavier phase of PVC for the sieve fraction 150–180  $\mu\text{m}$  of Neralit 652 for various  $\text{NaNO}_3$  concentrations can be seen in Figure 1. In all cases the rate of establishment of the volume of the specifically heavier phase and its magnitude increase with decreasing concentration of the testing solution used, in accordance with the increased solubility of air solutions with decreasing  $\text{NaNO}_3$  concentration. Figure 1 shows that the process of filling the pores is completed within 8 h, because values of the volume of the specifically heavier phase remain virtually unchanged even after 24 h. In the investigated PVC types both unfractionated and in their sieve fractions, the time dependency is similar to that in Figure 1 (the rate of establishment of the equilibrium volume of the specifically heavier PVC phase increases with decreasing  $\text{NaNO}_3$  concentration, and stationary values of the volume of specifically heavier phases are reached within 8 h of contact).

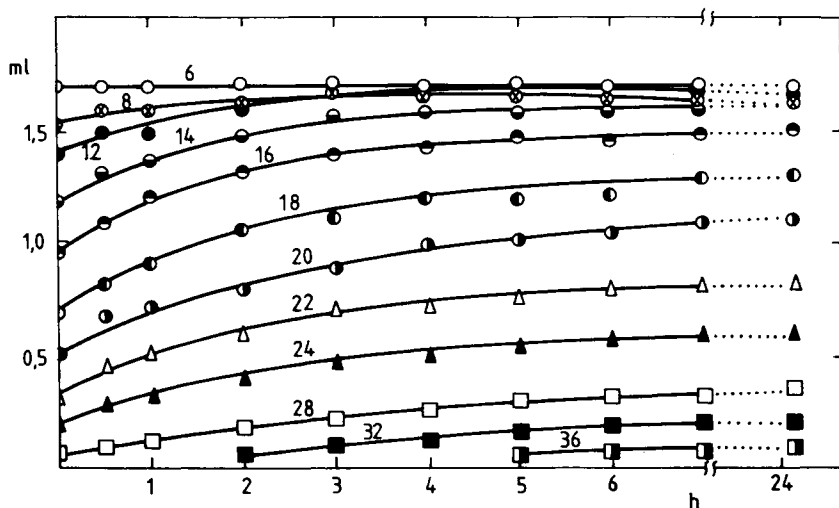


Fig. 1. Dependence of the volume of the specifically heavier PVC phase (mL) on time (h) for Neralit 652 (fraction 150–180  $\mu\text{m}$ ) at various  $\text{NaNO}_3$  concentrations (% , values at curves).

Figures 2 and 3 show both kinetic (after 1 h of contact) and equilibrium (after 24 h of contact) density curves of unfractionated PVC powder of Neralit 652, Neralit 702, and Neralit 702 FE and of their sieve fractions. Density curves are, in fact, cross sections in assemblies of the time dependences of volumes of the specifically heavier PVC phases for various concentrations (i.e., densities) of testing solutions at a chosen value of the independent variable, i.e., time. For the individual fractions they represent the dependence of the volumes of the specifically heavier PVC phases from standard weighed quantities (100 g) on the concentrations of the  $\text{NaNO}_3$  solutions for a chosen contact time.

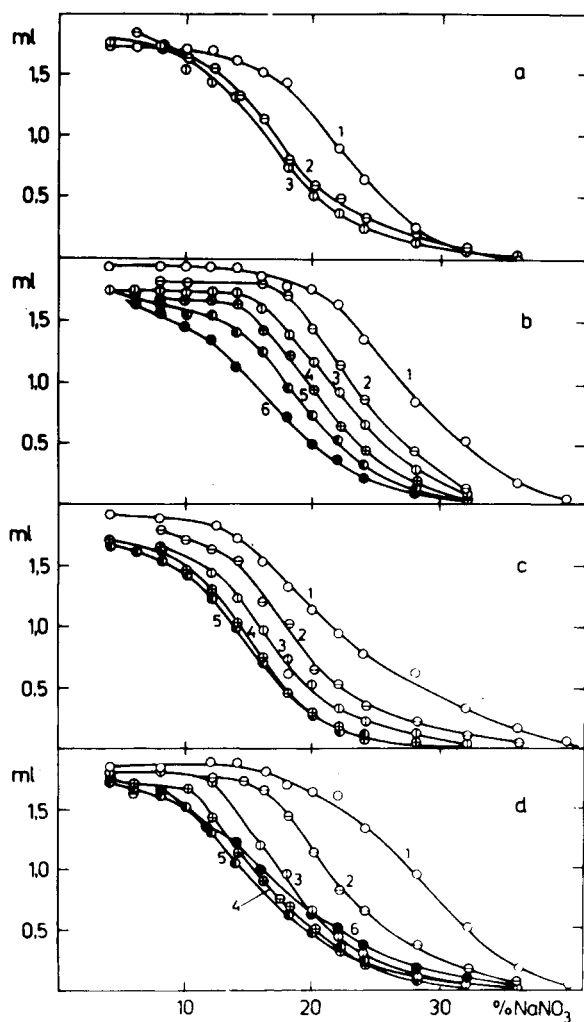


Fig. 2. Kinetic density curves (after 1 h of contact) as dependences of the volume (mL) of the specifically heavier PVC phase on the concentration of  $\text{NaNO}_3$  solution (%): (a) unfractionated samples: (1) Neralit 652; (2) Neralit 702; (3) Neralit 702 FE; (b) Neralit 652; (c) Neralit 702; (d) Neralit 702 FE [fractions of samples, size ( $\mu\text{m}$ ): (1) below 63; (2) 63–90; (3) 90–125; (4) 125–150; (5) 150–180; (6) above 180].

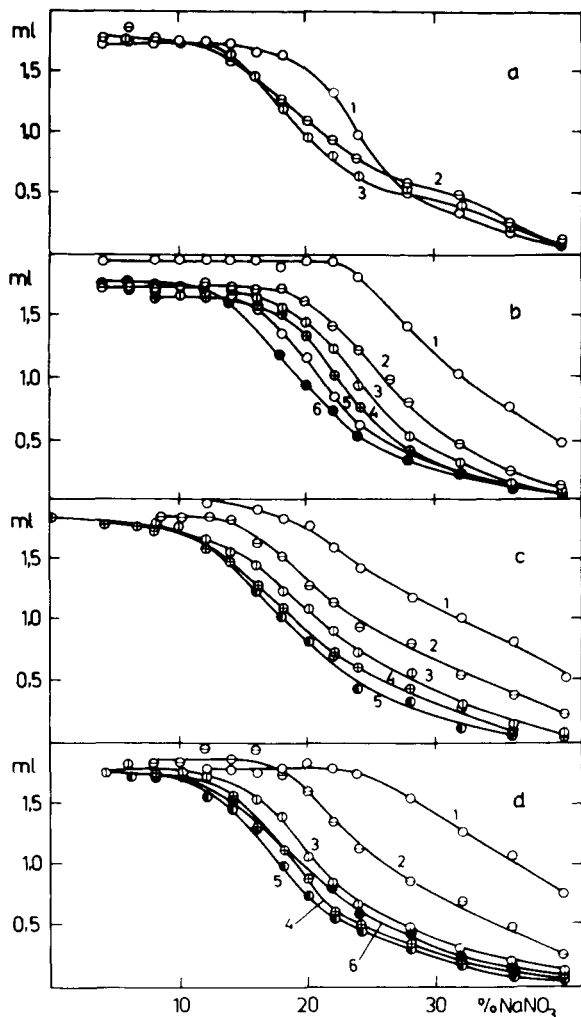


Fig. 3. Equilibrium density curves (after 24 h of contact) as dependences of the volume (mL) of the specifically heavier PVC phase on the  $\text{NaNO}_3$  concentration (%): (a) unfractionated samples: (1) Neralit 652; (2) Neralit 702; (3) Neralit 702 FE; (b) Neralit 652; (c) Neralit 702; (d) Neralit 702 FE [fractions of samples, size ( $\mu\text{m}$ ): (1) below 63; (2) 63–90; (3) 90–125; (4) 125–150; (5) 150–180; (6) above 180].

In the curves after 1 h [Figs. 2(a)–(d)] and 24 h [Figs. 3(a)–(d)], in all cases we can see a shift with time towards higher values of the  $\text{NaNO}_3$  concentration (= densities), which is in agreement with a gradual filling of the pores in PVC particles with the testing solution. The equilibrium curves have somewhat smaller slopes compared with the kinetic ones, which indicates a wider density distribution. In a more detailed comparison of the shape of close curves [e.g., (4) and (5) in Figs. 2(c) and 3(c) or in Figs. 2(d) and 3(d)], a somewhat better resolution in the case of equilibrium curves can also be perceived. Since the kinetic curves represent mutual relations between fractions and between various PVC types in a relative manner, both kinetic and equilibrium curves can be used in the mutual comparison of the quality of powders, or in the comparison of their quality with that of a corresponding

standard. At the given number of centrifuging test tubes the kinetic procedure is faster, but in this case the chosen time of contact must be respected as the decisive parameter. Curves starting from 8 h of contact are independent of time and provide a possibility for discerning with respect to the equilibrium density, and thus also inform about the total free volume inside the particle, which is inaccessible to the testing solution under the given conditions (closed pores and the like). For fractions of Neralit 652 with a grain smaller than 180  $\mu\text{m}$ , the specific surface area determined by the BET method is virtually independent of the particle size, and by its value ( $0.53 \text{ m}^2 \text{ g}^{-1}$ ) is about eight times larger than that ( $0.068 \text{ m}^2 \text{ g}^{-1}$ ) of hypothetical, spherical isometric nonporous PVC particles with the diameter 63  $\mu\text{m}$ , which by their size correspond to the mesh size of the smallest of the sieves used.

In the case of Neralit 652 [Figs. 2(b) and 3(b)], the particle density uniformly increases with a decrease in their size; the increased distances between the adjacent density curves for the finest and coarsest fractions are probably due to the wider spectrum of particle size compared with medium fractions. In comparison with Neralit 652 all the corresponding fractions of Neralit 702 [Figs. 2(c) and 3(c)] have a distinctly lower density. The increase in density of Neralit 702 with decreasing particle diameter is not uniform: The increments increase with decreasing particle size. In Neralit 702 FE, containing 36 fish eyes/1 g PVC compared with commercial Neralit 702, which does not contain any fish eye, there was an important shift towards larger particles at the expense of the medium fraction, and also in increase in the density of fractions, especially the finest ones. These results suggest that sieve analyses, along with the determination of density curves (especially in the finest fractions), may indicate the occurrence of fish eyes, particularly in fractions of fine and very fine grain size. A comparison with the standard sample of the same PVC type which satisfies the intended application is easy to perform.

The authors are indebted to Miss J. Nohová for careful experimental assistance.

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Received November 20, 1987

Accepted March 28, 1988