The Dependence of Kinetic Density Curves of Suspension PVC Powder on the Content of Defective Particles

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Synopsis

The method of kinetic density curves was used to investigate the sieve fractions of suspension PVC powder of the type Neralit S-682 with various content of difficult to process particles ("fish eyes"). It was found that by increasing the content of fish eyes, the effective density curves are shifted to lower density values. This finding can be utilized in the characterization and evaluation of sieve fractions of PVC.

INTRODUCTION

The difficult to process particles in powder of suspension poly(vinyl)chloride (PVC) are determined by a standard procedure: A thin film is prepared from a mixture of PVC powder, carbon black, plasticizer, and additives. On the black film thus formed, the unprocessible particles appear in the passing light as light points or "fish eyes"; the result of determination is measured by the number of fish eyes per one gram of PVC. A disadvantage of the standard method is that the difficult to process particles have a very small diameter, which may pose the basic obstacle in highly demanding optical applications, need not be measured in this manner. A number of methods have been reported in the literature which allow the quality of PVC powders to be estimated with respect to their homogeneity and the content of fish eyes.

Horáček and Pánková[1] separated these particles from normal ones using enrichment techniques based on fractionation of suspension PVC powders, partly swollen with dioctyl phthalate, by means of aqueous $ZnSO_4$ solutions of various density. Balakirskaya and Shtarkman[2] fractionated powders of suspension PVC for morphological investigation by means of a mixture of methanol and tetrachloromethane of various density. The same method was employed by Defife,[3] who used it as one method of characterization of the homogeneity of PVC powders and their suitability for a certain type of treatment. Along with the procedure just mentioned,[2] Defife also reports in his study a microscopic method consisting in the observation of gradual penetration of silicone oil inside the particles of suspension and block PVC. Homogeneity is estimated on the basis of the time dependence of the ratio of optically transparent and opaque fraction of the individual PVC grains subjected to the effect of silicon oil. In the same study, the homogeneity of PVC powders is characterized in a similar way, i.e., according to the uniformity of penetration of the solvent and to the decomposition of the grains into primary particles by means of quinoline.[3,4]

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In our papers[5] we have described the preparative and analytical separation of fractions with respect to the different effective density of suspension PVC powders and its utilization in the determination of density characteristics by density titration. In other studies,[6] we eliminated some shortcomings of the density titration and introduced the method of determination of density dispersion using kinetics density curves.

In this paper we examined the effect of the concentration of difficult to process particles in suspension poly(vinyl chloride) of the type Neralit S-682 on its characteristics expressed through effective densities, i.e., kinetic density curves.

EXPERIMENTAL

Polymer

The suspension powder poly(vinyl chloride) Neralit S-682 with various contents (1, 8, and 54) of fish eyes per gram PVC; filled samples were obtained from Spolana Neratovice.

Analyses

Sieve analysis of the samples was carried out using 500 g charges using normalized sieves 63, 90, 125, 150, and 180 μm in a Luftstrahlsieb Alpine apparatus.[5-7]

$NaNO_3$ solutions. The basic 40% solution was prepared by dissolving $NaNO_3$ (reagent grade, dried to constant weight) in degassed distilled water. Solutions of lower concentration were obtained by adding a calculated amount of degassed water to the weighed amount of basic solution.

Time dependence of the volume of the specifically heavier PVC fraction. To a weighed amount (1.00 g) of the sieve fraction of dry PVC powder in graduated centrifugation test tubes, 3.5 mL of solution having a chosen $NaNO_3$ concentration was added each time. The contents of the test tubes were stirred at 25°C, and after a specified time, the test tubes were centrifuged (centrifuge Chirota) for 5 min at 60 g, and the volume of specifically heavier PVC phases were recorded. The stirring, centrifugation, and recordings were repeated at predetermined intervals.

RESULTS AND DISCUSSION

In the granulometric evaluation of the samples, the masses of sieve fractions (g_i) were expressed in fractions (x_i):

$$x_i = g_i / \sum_{i=1}^{6} g_i \qquad (1)$$

and are given in Tables I–III along with the cumulative function $F(x_j) = \sum_{i=1}^{j} x_i$. The cumulative functions give the dependence of the mass fraction of particles,

TABLE I
Granulometric Analysis of Neralit S-682 with 1 Fish Eye/g PVC (500.00 g)[a]

Fraction no. (i)	Particle size (μm)	Weight of fraction (g_i)	Weight fraction (x_i)	Cumulative function $F(x_i)$
1	0–63	14.24	0.02886	0.02886
2	63–90	41.12	0.08333	0.11219
3	90–125	187.99	0.38098	0.49317
4	125–150	110.49	0.22392	0.71709
5	150–180	117.94	0.23902	0.95611
6	Above 180	21.66	0.04390	1.00000

[a] Losses due to manipulation and additional drying = 6.56 g = 1.3%.

the diameter of which does not go beyond the chosen value on the particle size (μm).

Figure 1 shows the cumulative functions for the analyzed samples, the average particle sizes and the values of statistical quantils were read off for the characterization of the width of cumulative function and its asymmetry. The average particle sizes D (d_{50}) are values on the x axis with the ordinate $F(x_i) = 0.50$. The statistical quantils (d_{16}, d_{84}) are values on the x axis, the ordinates of which are $F(x_i) = 0.16$ and $F(x_i) = 0.84$. The width of the cumulative function R (μm) is defined by

$$R = (d_{84} - d_{16})/2 \tag{2}$$

and the asymmetry of the cumulative function (A) is defined by

$$A = [(d_{84} - d_{50}) - (d_{50} - d_{16})]/(d_{84} - d_{16}) \tag{3}$$

With increasing fish eye content (Table IV), the average particle size and the distribution width decrease, though at a much slower rate than the average particle size. The asymmetry values of cumulative functions are positive with all samples, which means that the weight distribution of major fractions in the samples is somewhat broader than that with fractions having small diameters,

TABLE II
Granulometric Analysis of Neralit S-682 with the Content 8 Fish Eyes/g PVC (Weighed Amount: 500.00 g)[a]

Fraction no. (i)	Particle size (μm)	Weight of fraction (g_i)	Weight fraction (x_i)	Cumulative function $F(x_i)$
1	0–63	8.42	0.01716	0.01716
2	63–90	51.10	0.10413	0.12129
3	90–125	195.56	0.39850	0.51979
4	125–150	107.47	0.21900	0.73879
5	150–180	109.16	0.22243	0.96122
6	Above 180	19.03	0.03878	1.00000

[a] Losses due to manipulation and additional drying = 9.26 g = 1.9%.

TABLE III
Granulometric Analysis of Neralit S-682 with the Content 54 Fish Eyes/1 g PVC (Weighed Amount: 500.00 g)[a]

Fraction no. (i)	Particle size (μm)	Weight of fraction (g_i)	Weight fraction (x_i)	Cumulative function $F(x_i)$
1	0–63	17.12	0.03439	0.03439
2	63–90	65.79	0.13217	0.16656
3	90–125	227.58	0.45720	0.62376
4	125–150	88.24	0.17727	0.80103
5	150–180	92.32	0.18547	0.98650
6	Above 180	6.72	0.01350	1.00000

[a] Losses due to manipulation and additional drying = 2.23 g = 0.4%.

the more so the higher the content of fish eyes. The results suggest that a detailed wet sieve process analysis could be used as a guideline in the characterization of the quality of PVC already in the production cycle stage. In such a case, difficulties involved in the dry sieving of the samples and due to the electrostatic charge of the polymer would be removed.

The dependences of the volume of the specifically heavier PVC phase (mL) obtained from the standard weighed amount 1.00 g on the time of contact (h) of PVC powder with testing $NaNO_3$ solutions having the given concentrations (%) are shown in Figure 2 for various contents of fish eyes and various sieve fractions. Hence we can see that:

1. In all samples the rates of establishment of the volume of the specifically heavier phase increase with decreasing concentration of $NaNO_3$ solutions, due to the gradual dissolution of air in the $NaNO_3$ solution; the testing solution penetrates into the PVC particles, gradually filling in cavities and pores. The solubility of air decreases with increasing salt concentration in the solutions.

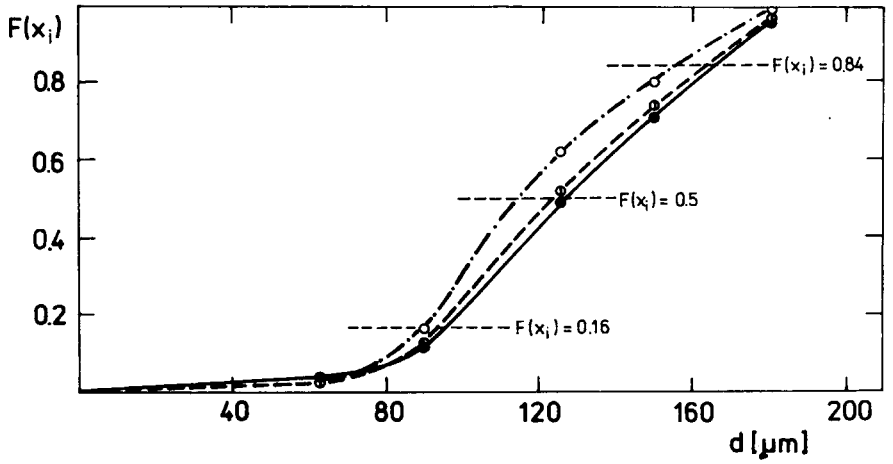

Fig. 1. Neralit S.682. Cumulative functions as dependences of weight fractions g/g of particles the diameter of which, d (μm), does not go beyond the chosen size: (●) 1 fish eye/g PVC; (⊙) 8 fish eyes/g PVC; (○) 54 fish eyes/g PVC.

TABLE IV
Granulometric Analysis of Neralit S-682 With Various Contents of Fish Eyes

Number of fish eyes (pieces/g PVC)	1	8	54
Average particle size D (μm)	127	123	113
Distribution width R (μm)	35	33.5	32.5
Asymmetry of distribution A	0.0857	0.1343	0.2923

2. The rate of establishment of the volume of the specifically heavier PVC phase is the faster the smaller the grain size of sieve fraction, because of shorter pathway of diffusion processes involved (i.e., penetration of testing solutions, dissolution of the air from the pores in solution, diffusion of the dissolved air through the liquid in pores out of the particle). In the original nonfractionated samples possessing a high inhomogeneity of the particle size, their behavior in the interaction with the $NaNO_3$ solution approaches fractions 125–150 μm, in the spite of the fact that this fraction is not the predominant one (in all samples, Tables I–III, the fraction 90–125 μm predominates, though its behavior is quite different).

3. In the time dependences of volumes of the specifically heavier PVC phase measured for low $NaNO_3$ concentrations, the initial quick increase in volume is sometimes followed by a monotonic decrease or by the formation of flat curves with a maximum. In such cases, those clusters of particles that survived the sieving procedure as agglomerates are sometimes broken up during the stirring; with increasing time, the PVC grains may become arranged more compactly than at the beginning. The condition for the formation of a function with a maximum consists in a higher rate of establishment of the volume of the specifically heavier PVC phase (i.e., filling in the pores in the particles), compared with the rate of disintegration of the clusters; this is best satisfied for the most dilute solutions.

From the curves in Figure 2, the dependences of the volume of specifically heavier phase (from the standard weight amount of sieve fraction of PVC = 1.00 g) on the concentration (in %) of testing solutions of $NaNO_3$ can be derived for the predetermined time(s) of contact by reading the corresponding volumes in various solutions and drawing the volume-concentration (dependences (see e.g., Fig. 3). Since, at constant temperature, the density of $NaNO_3$ solutions is an unambiguous function of its concentration, the curves thus obtained represent in the implicit form, effective (this means dependent on the history of a sample's contact with testing solution), dynamic density curves for the given sieve fraction and the chosen time of contact.

The data in Figure 2 allow us to construct effective density curves within the measured interval for any contact time. Figure 3 shows the density curves for the sieve fraction 125–150 μm of Neralit S-682 containing 8 fish eyes/g PVC for various times of contact (0.5, 1, 3, 5, 1, and 24 h). As expected, due to the gradual filling-in of the pores with the testing solution, the density curves are shifted with increasing time of contact toward higher effective density values (i.e., toward higher $NaNO_3$ concentrations). To compare various fractions and samples, from the set of density curves in Figure 3, we chose the time cut after 30 min. The reason was the short duration of the experiment and the good resolution of the effective densities of individual samples and fractions.

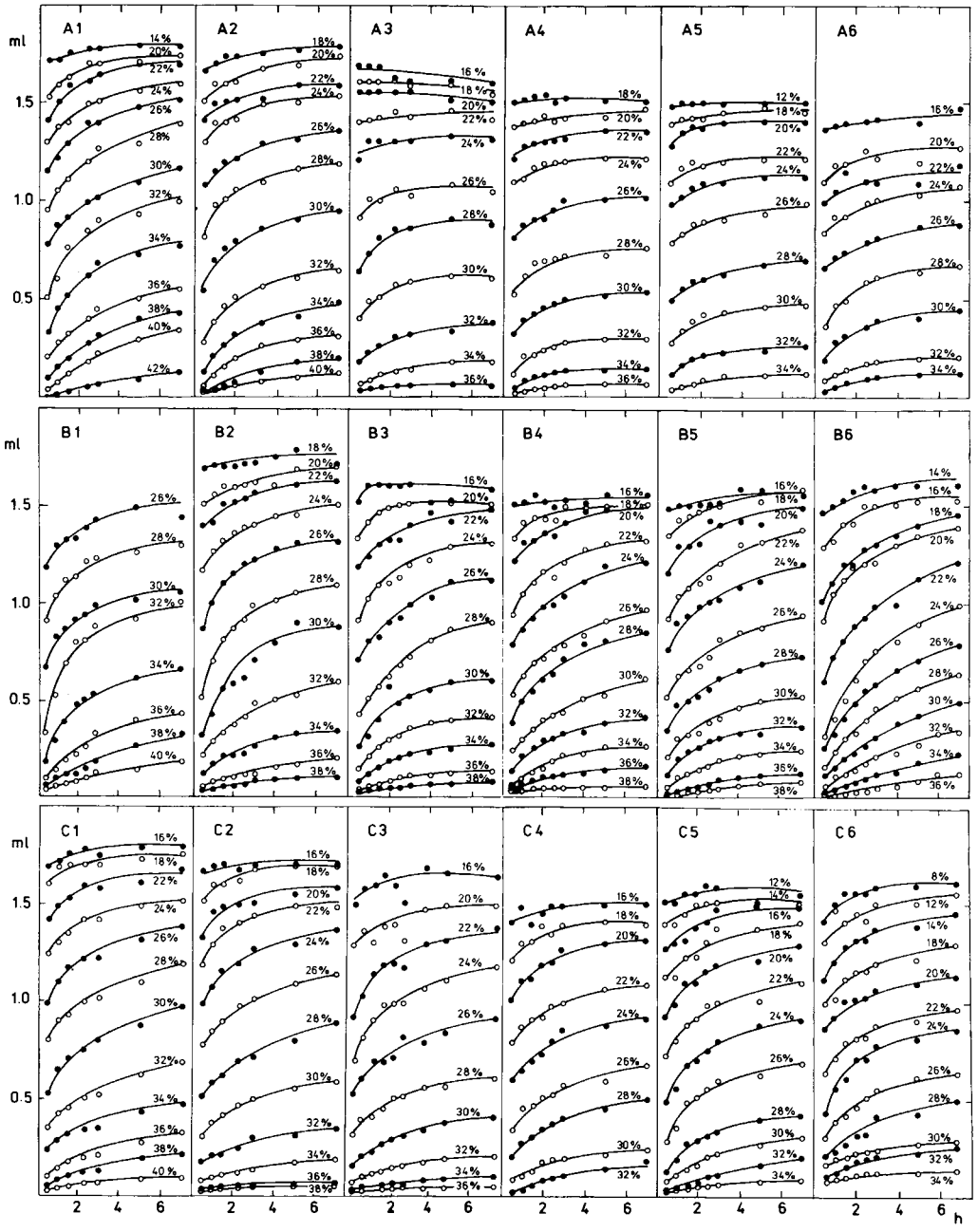

Fig. 2. Dependence of the volume of the specifically heavier PVC fraction (mL) obtained from standard weighed amount 1.00 g on the time of contact (h) in $NaNO_3$ solutions of the given concentration (%) for sieve fractions. (1) 0–63 μm, (2) 63–90 μm, (3) 90–125 μm, (4) 125–150 μm, (5) 150–180 μm, and (6) above 180 μm of Neralit S-682 containing (A) 1 fish eye/g PVC, (B) 8 fish eyes/g PVC, and (C) 54 fish eyes/g PVC.

Figure 4 summarizes the effective kinetic density curves for the sieve fractions 0–63, 63–90, 90–125, 125–150, 150–180, and above 180 μm for Neralit S-682, containing 1, 8, and 54 fish eyes in one gram PVC. In all cases in the corre-

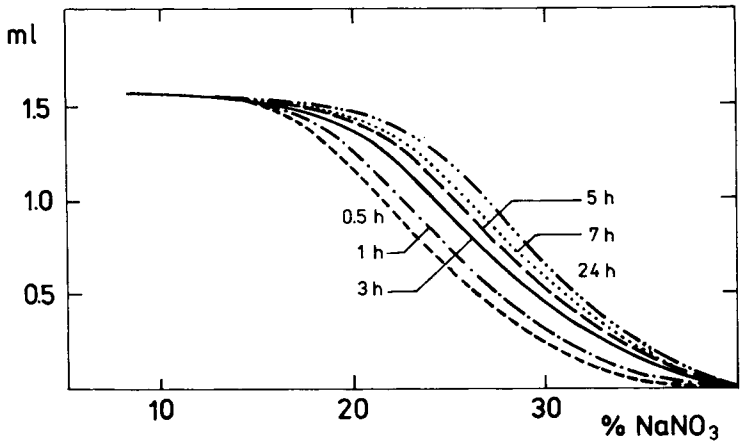

Fig. 3. Neralit S-682 containing 8 fish eyes/g PVC, fraction 125–150 μm. Dependence of the volumes of the specifically heavier PVC phase (mL) obtained from the standard weighed amount 1.00 g on the concentration of $NaNO_3$ (%) for various times (0.5, 1, 3, 5, 7, and 24 h) of contact between PVC and $NaNO_3$ solutions.

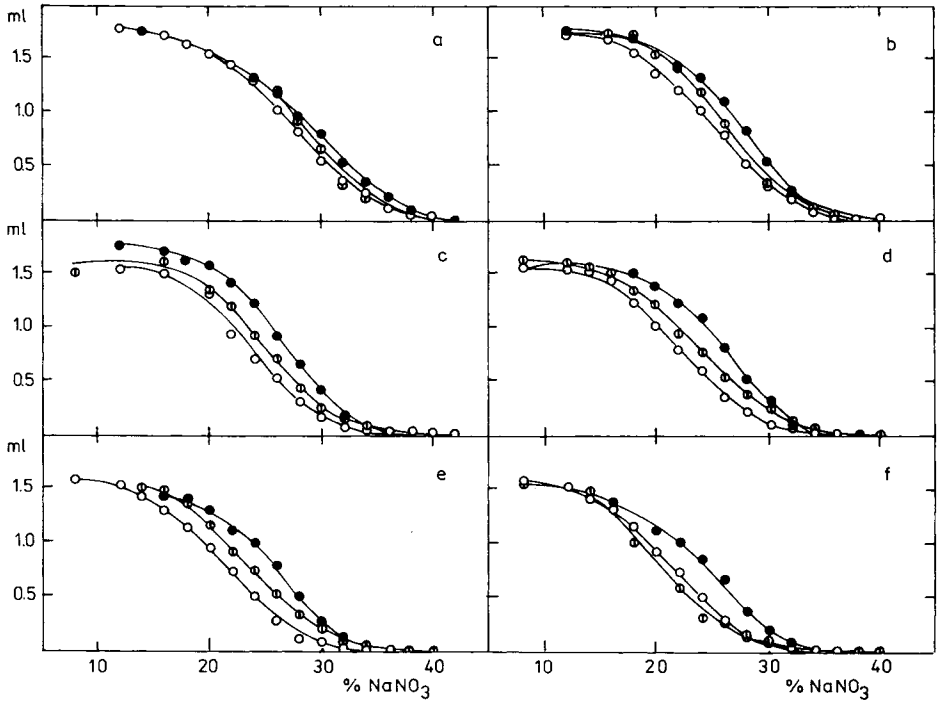

Fig. 4. Dependence of the volume (mL) of the specifically heavier PVC phase from the standard weighed amount 1.00 g on the concentration (%) of $NaNO_3$ for sieve fractions: (a) 0–63 μm, (b) 63–90 μm, (c) 90–125 μm, (d) 125–150 μm, (e) 150–180 μm, and (f) above 180 μm of Neralit S-682 containing (●) 1 fish eye/g PVC, (Φ) 8 fish eyes/g PVC, and (○) 54 fish eyes/g PVC.

sponding sieve fractions, the samples with one fish eye/g PVC, 8 fish eyes/g PVC, and 54 fish eyes/g PVC possess, respectively, the highest, medium, and the lowest effective densities. With decreasing particle size (due to the faster kinetics of filling-in the pores) the curves are displaced toward higher values of effective densities, and thus also of the $NaNO_3$ concentrations. In Figure 4(f), in the case of the fraction above 180 μm, the density curve for the sample with 8 fish eyes/g PVC is shifted compared with the sample with 54 fish eyes/g PVC, because the sieve fractions above 180 μm are limited in their size only from the bottom (by mesh size of 180 μm sieve), but they are not restricted from above (unlike the preceding fractions), and also due to the higher content of artifacts (irregular particles, clusters, intergrown formations, and the like).

CONCLUSIONS

The method of determination of kinetic density curves allowed samples of suspension PVC powders with various content of fish eyes to be described and compared with each other.

On the basis of the data obtained, the use of solutions in the concentrations range 20–30% $NaNO_3$ can be advantageously recommended for testing sieve fractions of Neralit S-682. With very fine and fine fractions, concentrations up to 33% can be considered, while for rougher fractions a concentration starting from 17% $NaNO_3$ seems to be the right choice. Density dispersions found for samples of powders of Neralit S-682 with a known content of fish eyes make possible a good characterization of sieve fractions of the dry polymer of the same type by comparing them with the density dispersions of standards, either by a one-point method or by employing a kinetic procedure. The characterization of samples with particles polydisperse as to their size, although theoretically feasible, depends nevertheless on the knowledge of weight distribution with respect to the particle size of the sample under study.

The determination does not require complicated equipment and may be used in scientific and industrial laboratories in the characterization of suspension powder polymers, or in an estimation of the quality of the particular production charges.

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