

Size Analysis of Polymer Latex Powder. Comparison of Results Obtained by Means of the I.C.I.-Joyce, Loebel Disk Centrifuge, the Coulter Counter, and the Electron Microscope

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Synopsis

The volume frequency size distribution of PVC latex powder was determined by means of three different methods, which all gave the same frequency maximum at about 0.8–0.9 μ diameter. While the electron microscope analysis, which allows the agglomerates to be resolved into individual primary particles, did not show any particles above 1.5 μ in a sample of 9000, both the Coulter counter and the disk centrifuge showed a considerable amount of larger particles.

INTRODUCTION

In connection with process studies on emulsion polymerization, it was desirable to get a measure of the size distribution of the latex particles. As the particle diameters were generally below 1 μ , usual particle sizing equipment such as the Andreasen pipet and sieves could not be used. Several different principles and instruments were considered and finally two of the most promising, the Coulter counter and the disk centrifuge, were tested with a poly(vinyl chloride) (PVC) latex powder, for which the size distribution had previously been determined by electron microscopy. The work on the Coulter counter as well as the electron microscopy was carried out at the Chr. Michelsen Institute, whereas the part of the work concerning the disk centrifuge was done by Jones and co-workers (Joyce, Loebel & Co., Ltd., England).

EXPERIMENTAL

Electron Microscope

A sample from the test powder was mounted on an electron microscope grid by the collodion fixing technique.¹ This technique makes it possible to obtain a nearly random distribution of the particles across the grid area. About 9000 primary particles were counted and sized on photomicrographs of known magnification. The number-frequency histogram was converted

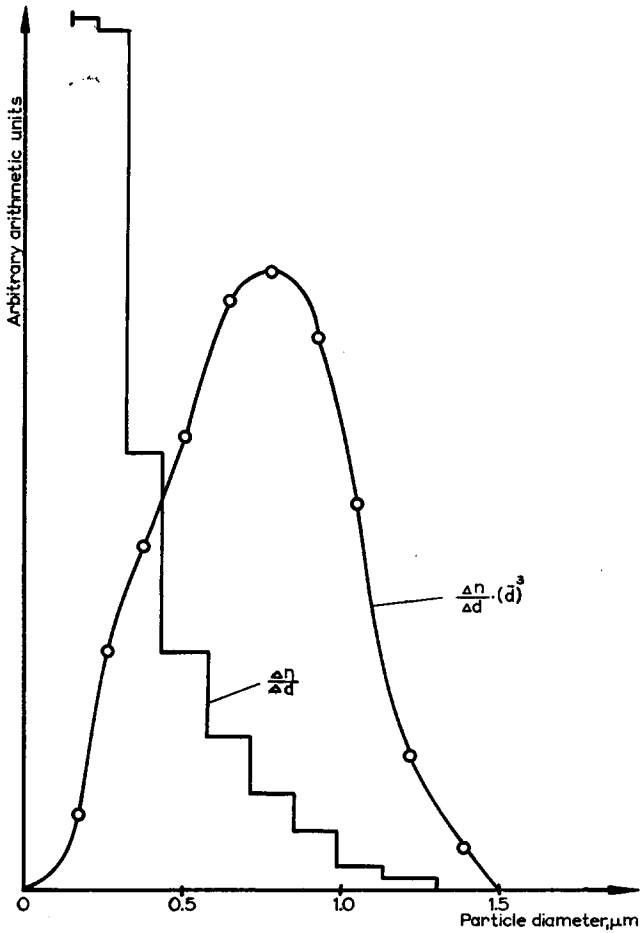


Figure 1.

into a volume-frequency curve by multiplying the number frequency of each histogram column by $(\bar{d})^3$, where \bar{d} is the mean diameter in the respective histogram class. The results from the analysis of the test powder are given in Figure 1.

Disk Centrifuge

Stable sedimentation was realized by using a 4% suspension of the sample powder in distilled water. Texafor D40 was used as a dispersing agent and Lissapol N as a wetting agent. The suspension was agitated by means of an ultrasonic probe system for 15 sec. before each operation of the centrifuge. The spin fluid used was a glycerol-distilled water solution.

The centrifuge was operated by applying the Joyce Loebel buffered line start technique⁴ with 1 ml. of distilled water as the buffer layer. For each particle size, 0.5 ml. of the sample suspension was injected onto 30 ml. of

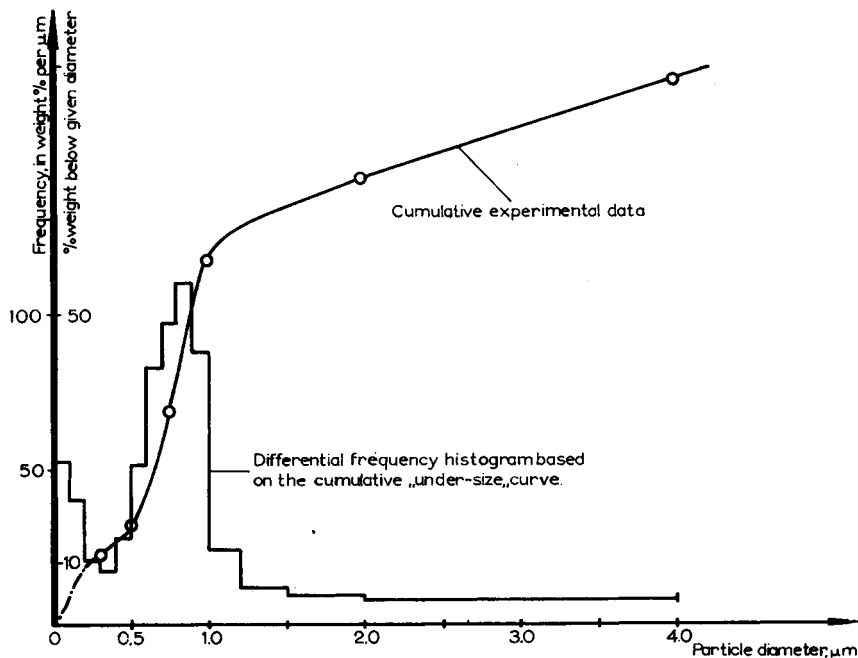


Figure 2.

the buffered spin fluid. The collected undersize fractions consisted of particles up to the size programmed for in 25.5 ml. of spin fluid.

The probe system was washed through with two 5-ml. volumes of spin fluid into the 50-ml. volumetric collection flask, which was then filled up to the graduation with more spin fluid.

Three reference samples were produced by taking 0.5 ml. of the suspension and injecting it straight into the 50-ml. volumetric flask and filling to the graduation with spin fluid. These references contained the whole of the particle size range.

A special technique was applied for the analysis of fractions. The technique² consists of a coagulation process, filtering through previously weighed sintered glass elements, drying and weighing.

The average weight of the reference fractions was equated to 100% and thus the weights of PVC in each cut fraction gave the percentage cumulative undersize weights, which were then plotted against particle size to produce the distribution curves shown.

The results from the disk centrifuge analysis of the test powder are given in Figure 2.

Coulter Counter, Model A

A few milligrams of the powder were well dispersed in absolute ethyl alcohol in a test tube by means of ultrasonic energy. A few drops of the

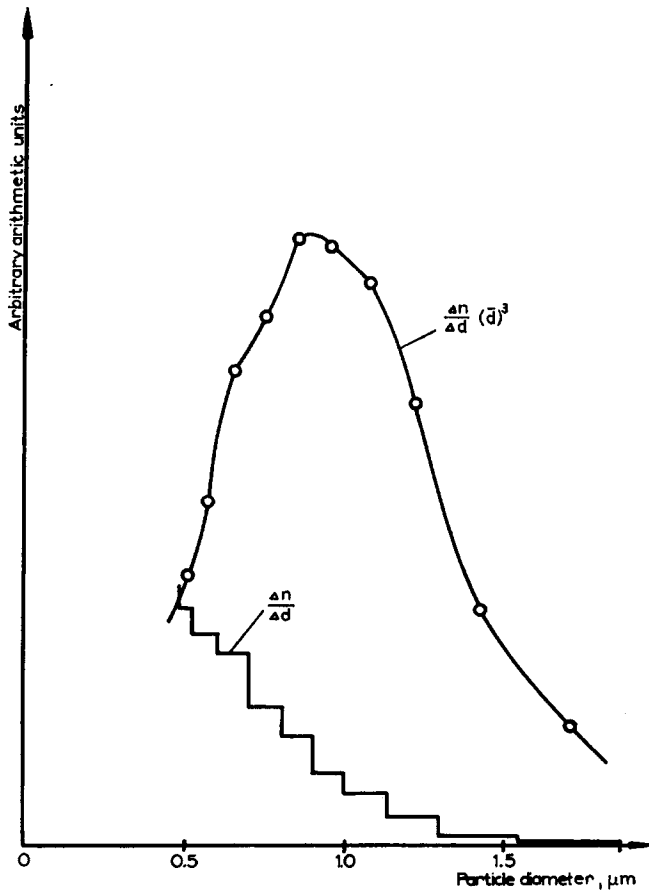


Figure 3.

dispersed concentrate were transferred to the electrolyte baker under agitation. The agitator was stopped during the analysis to avoid interference pulses. Because of the negligible sedimentation velocities of low density particles of about 1μ size, agitation was found to be unnecessary for keeping the particles in suspension during the relatively short period of analysis.

The technical conditions of the analysis were as follows: electrolyte, $0.8M$ aqueous NaCl solution, previously filtered through a 0.22μ Millipore membrane filter; dispersing agent, absolute ethyl alcohol; dispersing energy, ultrasonics; gain, 6; current, 9; range of threshold potentiometer, 0–1000; aperture diameter, 30μ ; manometer volume, 0.05 cm.^3 ; calibration constant, 0.194 (refers to the instrument settings above and does not include the F factor); maximum particle count at lowest threshold level, ca. 50,000. The results from the Coulter counter analysis of the test powder are given in Figure 3.

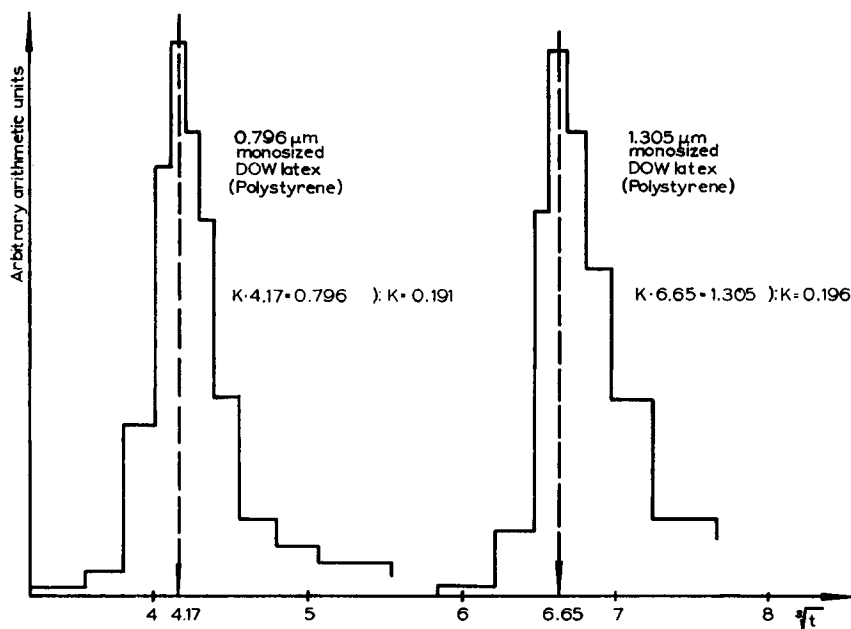


Figure 4.

The threshold scale was calibrated by counting and sizing two different samples of polystyrene Dow latex with very narrow size distributions. The polystyrene latices were dispersed and analyzed according to the procedure described above for the test powder. The latices were not measured electron-optically at the Chr. Michelsen Institute and the figures 0.796 and 1.305 μ are those given by the manufacturer (The Dow Chemical Company, USA).

The results from the calibration experiments, which were carried out at the same instrument settings as used for the analysis of the sample powder, are given in Figure 4. It is seen that the two calibration constants are very close to each other. Repeated experiments showed that these values were reproducible. In the analysis, the value $k = 0.194$, which is the mean k of the two calibration experiments given in the diagram, was used.

DISCUSSION

The electron microscope analysis involves at least three different types of possible errors. On the first hand, the microscope magnification cannot be specified more closely than, say, $\pm 3\%$. The consequence of this is that the diameter scale will be contracted or expanded correspondingly. The shape of the distribution curve is not affected by the magnification error. Secondly, the particles must not be affected by the electron beam in such a way that deformation, shrinking, or even melting takes place. Such effects occasionally have been observed in electron microscopy of other latices,

but not in connection with the particular latex mentioned here. Finally the sample which is counted and sized must be a random sample, containing the different particle sizes in the right proportions to give a correct picture of the size distribution. This implies that the total particle number counted must be sufficiently large. Repeated analysis of the present test sample have shown that in this case the errors mentioned are satisfactorily small to be neglected.

The frequency histogram from the disk centrifuge data is based on six cumulative points, which is too few to give a reliable continuous cumulative curve. However, it is clear that the frequency maximum occurs somewhere between 0.5 and 1.0 μ , which corresponds with the electron microscope data. It seems as if the 0.3 μ value is too large, giving rise to a second maximum towards zero diameter, which did not occur in the curve from the electron microscope analysis. It is also seen that the frequency does not come down to zero at about 1.5 μ . The reason for this is supposed to be the presence of stable agglomerates, which had not been destroyed by the ultrasonics, and which in the electron microscope could be resolved in individual primary particles.

The Coulter counter does not give any data below about 0.5 μ , which seems to be the limit in the fine end according to the equipment actually used. The volume frequency maximum appears at a slightly larger diameter than that of the electron microscope curve. Although this difference of about 0.1 μ is negligible, it coincides with the general impression that the Coulter counter in some cases gives slightly coarser size distributions than those obtained from electron microscopy of identical powders. It is further observed from Figure 1 that the Coulter counter volume frequency does not come down to zero at about 1.5 μ which would be expected from the electron microscope curve. The reason for this is supposed to be the same as for the similar effect in the disk centrifuge analysis, namely the presence of stable agglomerates. The reason why the Coulter counter analysis was not carried further than about 1.8 μ in the coarse end is quite incidental, and of course the analysis could have been continued up to 8–9 μ simply by using the gain and current switches.

CONCLUSIONS

In the case discussed here, both the disk centrifuge and the Coulter counter give volume-frequency curves with peak diameters approximately equal to that of the electron microscope curve.

However, while the electron microscope is capable of resolving the different primary particles in agglomerates, such agglomerates in the case of the two other methods will be detected as large single particles. Complete dispersion of the particles is therefore a necessary requirement if reliable primary particle distributions are to be measured by the disk centrifuge or with the Coulter counter.

In the present case of polymer latex, the two methods seem to have the same lower size limit at about 0.5μ .

The disk centrifuge has the advantage of giving the complete cumulative weight distribution as primary information, while the Coulter counter requires some sort of extrapolation of the frequency distribution in the fine end³ to give a cumulative percentage distribution.

On the other hand, the Coulter counter method seems to be far more rapid than the disk centrifuge technique, in particular if a computer is used in calculating the distribution from the primary data.

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References

1. R. K. Eckhoff, *Microscope & Crystal Front*, **14**, No. 12, 490 (1965).
2. Rutherford Technical College, Newcastle-upon-Tyne, England, private communication.
3. R. K. Eckhoff, *Nature*, **210**, 765 (1966).
4. *Special Techniques to Obtain Stable Centrifugation of Particulate Systems*, Joyce, Loebel, England.

Résumé

La distribution de grandeur de fréquence de volume d'un poudre de PVC-latex a été déterminée au moyen de trois méthodes inégales, qui ont toutes les trois donné le même maximum de fréquence de $0.8-0.9 \mu$ de diamètre environ. L'analyse faite par le microscope-électron, permettant aux agglomérats de dissoudre en particules individuelles primaires, n'a présenté aucune particule au dessus de 1.5μ dans un échantillon au nombre de 9000. La méthode de Coulter Counter ainsi que la méthode de Disc-Centrifuge ont d'autre part présenté une quantité considérable de particules plus grandes.

Zusammenfassung

Die Volumendichtefunktion eines PVC Latex-Pulvers wurde durch drei verschiedenen Methoden bestimmt. Alle drei Methoden ergaben dieselbe maximale Volumendichte bei etwa 0.8 bis 0.9μ Diameter. Der Coulter Zähler und die Scheibenzentrifuge zeigten eine ansehnliche Menge von grösseren Partikeln, während die elektron-mikroskopische Analyse, die eine Auflösung von den Agglomeraten in individuelle Primärpartikeln ermöglicht, keine Partikeln über 1.5μ in einer Probe von 9000 zeigte.

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