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APPARATUS FOR USE IN DETERMINING PARTICLE SIZE AND DISTRIBUTION OF PARTICLE SIZE

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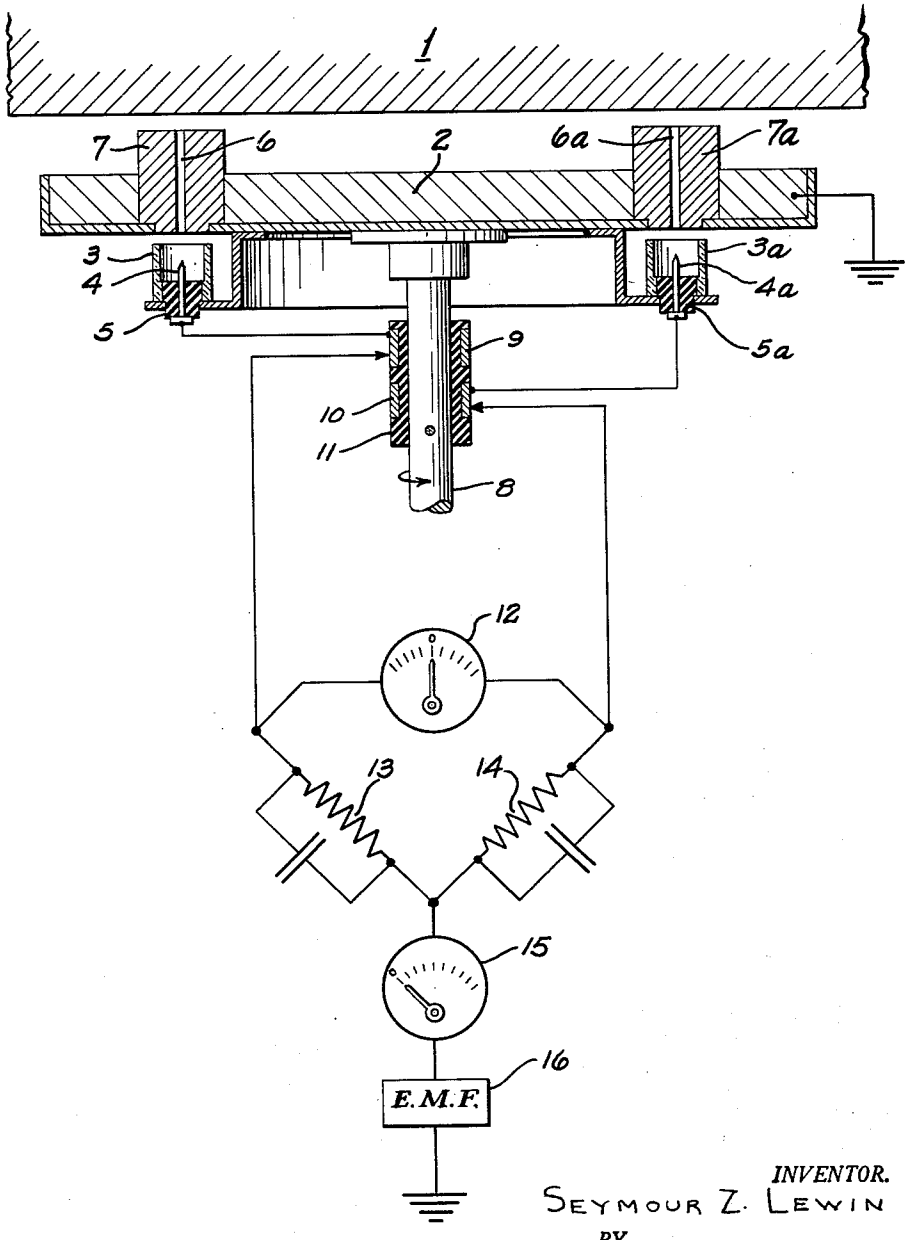

INVENTOR.
SEYMOUR Z. LEWIN
BY
Morgan, Finnegan, Durham & Pine
ATTORNEYS.

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APPARATUS FOR USE IN DETERMINING PARTICLE SIZE AND DISTRIBUTION OF PARTICLE SIZE

Seymour Z. Lewin, New York, N.Y., assignor to Evans Research & Development Corporation, New York, N.Y., a corporation of New York

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This invention relates to a novel method and apparatus for determining the size of particles and/or the distribution of particle size in compositions which have randomly distributed particles.

During the past two decades, industry has extensively adopted rapid, instrumental methods of testing for the purpose of improving manufacturing processes and controlling the characteristics of finished products. These methods have permitted processes to be carried out more rapidly and economically, and yet the products meet specifications with greater precision than ever before. One area of measurement that has advanced far less than most others is the measurement of particle size and particle size distribution in compositions containing randomly distributed particles such, for example, as powders, emulsions, gels, aerosols, etc.

Prior to this invention a number of methods and apparati have been used for obtaining information about particle size. For example, ultramicroscopic, turbidimetric, X-ray diffraction, permeability and gas adsorption methods employing appropriate apparatus have been used for determining average particle size. Methods which have been used to determine particle size distribution include microscopic, electron microscopic, sieving, centrifuging, ultracentrifuging, elutriation and sedimentation methods.

The aforementioned prior art methods in current use suffer from at least one and in many cases a number if not all of the following disadvantages:

(1) They are time-consuming and tedious, requiring considerable expediture of manpower.

(2) They are imprecise and of poor resolution.

(3) They are severely limited in range.

(4) They require the removal of samples from the specimen.

(5) There is a long time delay between the removal of the sample and the production of the final data.

Objects and advantages of the invention will be set forth in part hereinafter and in part will be obvious herefrom, or may be learned by practice with the invention, the same being realized and attained by means of the steps, methods, combinations and improvements pointed out in the appended claims.

The invention consists in the novel steps, methods, combinations and improvements herein described.

It is an object of this invention to provide a new approach to determination of particle size and/or distribution of particle size in compositions having randomly distributed particles. A further object of this invention is to provide a novel method for determining particle size and/or distribution of particle size in compositions having randomly distributed particles in a more simple, economical and efficient manner than heretofore used methods. Yet a still further object of this invention is to provide a novel particle size analyzer which is simple in construction for use in determining particle size and/or distribution of particle size in compositions having randomly distributed particles. A still further object of this invention is to provide a novel method for determining particle size and/or distribution of particle size in a composition having randomly distributed particles without having to physically remove samples from said composition.

Another object of this invention is to provide a novel apparatus for use in determining particle size and/or distribution of particle size in a composition having randomly distributed particles without having to physically remove samples from said composition.

This invention is based on the discovery that valuable information for use in determining particle size and/or distribution of particle size in a composition having randomly distributed particles can be realized by obtaining data with respect to a number of different samples of said composition having the same predetermined volume, and subsequently observing the fluctuations in the data relating to said different samples of the same volume.

More particularly, in determining particle size and/or distribution of particle size in compositions having randomly distributed particles, data is obtained with respect to different samples of the same volume of a composition having known particle size and/or distribution of particle size. This data serves as "calibration data." Data is also obtained on different samples of the same volume of the composition under consideration of unknown particle size and/or distribution of particle size. This data serves as "specimen data." The volumes of the aforementioned samples on which calibration data and specimen data are obtained are the same. The data obtained is then compared and interpreted using calibration techniques whereby ultimately the particle size and/or particles size distribution of the composition under consideration may be determined. As indicated hereinbefore, the fluctuations in the calibration data are compared with the fluctuations in the specimen data as will be explained more in detail hereinbelow. A fluctuation is defined as the difference in magnitude of two independent measurements made on samples of precisely equal volumes. Of course as is well known to those familiar with calibration techniques, the accuracy of the results obtained is dependent upon the sufficiency of the data with respect to sample volumes of both known and unknown particle sizes and/or particle sizes distribution. Also, for reasons that will be evident hereinlater, in order to obtain sufficient data, it is important that data with respect to samples of different volumes be obtained.

The instant invention provides a novel method and apparatus whereby data of the aforementioned type may be obtained with respect to samples of compositions having known and unknown particle size and/or particle size distribution. Preferably, such data is obtained without having to physically remove samples from such compositions. More particularly, it has been found that data relating to particle size and/or particle size distribution may be obtained with respect to a sample of predetermined volume in a compositon having randomly distributed particles, said sample being referred to hereinafter as the "sampling," by:

(1) Applying to the composition under consideration, hereinafter referred to as the "specimen," a source of radiation to pass a radiation beam through at least a portion of the specimen, which beam is sensitive to the several phases of the specimen in the path of radiation;

(2) Controlling the area and depth of penetration of the radiation beam into the specimen, thereby attenuating said radiation beam; and

(3) Measuring the extent of attenuation to provide data with respect to a sampling of the specimen of a predetermined volume useful for comparison purposes in the manner discussed hereinabove in detail.

More particularly, as pointed out above, in the first step of the method of this invention, a source of radiation is applied to the specimen. Regardless of the source of radiation employed, it is essential that it possess the following characteristics with respect to the specimen:

(1) The source of radiation must physically interact

with specimen so as to pass a radiation beam through at least a portion of the specimen, which radiation beam is sensitive to the several phases of the specimen in the path of radiation. In other words, the source of radiation should not be very weakly or very strongly absorbed by the specimen so that it would be impossible to measure with reasonable accuracy the attenuation produced by the specimen.

The preferred source of radiation is a radioisotope. Radioisotopes which are beta emitters are preferred because in addition to fulfilling the aforementioned requirements, they also: (*a*) provide the desired radiations without requiring the use of expensive and bulky instrumentation, (*b*) are sources of radiation of substantially constant intensity, subject only to the precisely calculable decay curve, and (*c*) are available at low cost in high specific activity and in a safe, easily shielded form.

The following Table I discloses a list of well known radioisotopes useful as the source of radiation in accordance with the present invention. The data reported in Table I gives the maximum beta energy and the half-thickness for absorption in water for each of the radioisotopes listed in Table I.

Table I

Isotope	Maximum Beta energy (mev.)	Half-thickness (microns)
H^3	0.0189	0.5
C^{14}	0.155	24
S^{35}	0.167	29
Ca^{45}	0.255	60
Tc^{99}	0.296	75
Tl^{204}	0.762	275
Cl^{36}	0.716	400
P^{32}	1.708	1050
Y^{99}	2.275	1625

The depth of penetration of the radiation beam is controlled by the characteristics of the specimen in the path of the radiation beam as well as the energy spectrum of the radiation emitted by the source of radiation. As indicated heretofore, the radiation beam is attenuated and the extent of attenuation measured using conventional techniques such, for example, as the technique of back-scatter measurement or the technique of absorption (transmission) measurement. The volume of the sampling involved in the measurement is determined by the area irradiated by the radiation beam, the depth of penetration of the radiation beam and the effective portion of the radiation beam that is attenuated.

Reference is now made to FIG. 1 of the drawing which illustrates schematically one embodiment of an analyzer of the present invention useful in determining particle size. In the embodiment shown, the means for measuring the extent of attenuation of the radiation beam is a back-scattering measuring instrument.

Referring to FIG. 1, specimen **1** which may be of any composition having randomly distributed particles such, for example, as an emulsion, powder, gel, etc., is irradiated by a suitable source of radiation such, for example, as a tritium source **2**. The specimen is viewed in the back-scattering position by detector means through aperture means. The detector means comprises detectors **3** and **3a** which include electrodes **4** and **4a**, respectively, surrounded by insulation **5** and **5a**, respectively. The aperture means are provided by pinhole apertures **6** and **6a** in blocks **7** and **7a**, respectively, made of radiation absorbing material. The entire assembly of the radiation source, the detector means, and the aperture means are supported on rotatable shaft **8** on which are mounted collector rings **9** and **10**. Collector rings **9** and **10** are insulated from shaft **8** by insulation bushing **11**. Alternatively, the entire assembly may be stationary and means provided for rotating the specimen.

While two detectors **3** and **3a** are shown in order to obtain data with respect to two samples simultaneously, only one detector and aperture is required. Each of the detectors views a small sample volume in the specimen, the volume of the sample viewed depending upon the size of the corresponding aperture. The detectors **3** and **3a** are allowed to count or integrate the back-scattered betas for a sufficient time to reduce the counting random error to a suitably low value. If the tritium source is of high intensity (e.g. of the order of a curie), this counting time may be as short as a few seconds.

For example, tritium-zirconium sources are available having an activity of the order of 1 curie per cm.^{2}. If one-half this number is taken as the density of irradiation of the specimen surface, and that surface is viewed, in the back-scattering arrangement, through a 0.1 mm. aperture, the activity passing into the aperture would be $(\frac{3}{4})(1\times10^{-4})$ $(0.5\times3.7\times10^{10})$ $\%$ BS=ca $10^6\times\%$ BS d/sec. The symbol % BS means the fraction of the incident beam that is back-scattered. The symbol d/sec. means disintegration per second. Hence, a change (e.g. fluctuation due to sampling volume effect) of 0.0001 (i.e., a change of one part in ten thousand) in the back-scattering corresponds to a change in activity of 100 d/sec. at the detector.

As seen from the device of FIG. 1, electrical means are provided to convert the beta rays to current which may be measured to provide the data required for comparison purposes. In the particular embodiment shown, the difference in integrated detector currents is measured by meter **12**, which responds to the voltage difference between the two dropping resistors **13** and **14**. The meter **15** measures the total detector current. Meters **12** and **15** are operated by voltage source **16**. The difference in voltage on meter **12** is due to the randomness in the distribution of particles in the sampling volume together with the statistics of radioactive counting. However, the latter factor can be minimized by appropriate choice of the total integrated count so as to make the reading on meter **12** principally a measure of the sampling randomness. In operation, the assembly is allowed to count for the necessary time at a given position, and the readings on meters **12** and **15** are recorded; then the assembly is rotated about its axis and new readings are taken. This may be repeated as many times as desired; the greater the number of readings, the better the accuracy of the results. The average of the readings on meter **12**, disregarding the sign of the deflection, is proportional to the half-width of the Gaussian distribution referred to hereinbelow. The ratio of this to the reading on meter **15** is proportional to the relative fluctuation. This parameter is related to the concentration of particles in a certain size range, determined by the geometry of the apparatus. This range corresponds to the totality of particles from the largest down to a characteristic minimum size.

The embodiment of FIG. 1 may be simplified wherein only one detector is employed. In such instance the meter **12** is eliminated and the only current measuring instrument employed would be meter **15** which would measure the detector current produced by the back-scattering of beta beams scattered by one sample of predetermined volume. The detector or detectors employed are preferably windowless proportional counters through which Q-gas is circulated (cf. Karraker, D. G., DP–34, December 1953), although other standard components, such as ionization chambers, scintillation counters, etc., may be used.

While the embodiment of FIG. 1 illustrates an apparatus employing a back-scattering measurement instrument, it should be realized that other equivalent measuring techniques may be used. Accordingly, a particle analyzer may be used predicated on transmission measurements, rather than back-scattering measurements. In this case the detector means and the aperture means

are placed on the far side of the specimen, compared to the radiation source.

As indicated hereinbefore, the apparatus of FIG. 1 provides a unit for obtaining data with respect to the cumulative particle sizes over a specific range of particle sizes. If it is desired to obtain information data about the distribution of particle size in a specimen, a number of units of the type illustrated by the unit of FIG. 1 may be employed, the various units differing only with respect to the energy spectrum of the source of radiation and the aperture diameter. Each unit yields information data about the concentration of a different range of particle size. Alternatively, a single unit may be used having a variable detector aperture that changes in diameter on a programmed basis, in accordance with the range of particle size under investigation. This variable aperture programming can be achieved by meachanical, electrical, or magnetic means.

The principles of this invention are applicable to any composition having randomly distributed particles. While the method and apparatus of this invention are not limited to any theory of action, the following discussion is for the purpose of providing a complete understanding of how the method and apparatus of this invention are useful in analyzing compositions having randomly distributed particles with respect to particle size and particle size distribution.

The principles of this invention are readily applicable to both monodisperse systems and polydisperse systems. In the following discussion of monodisperse systems, spherical symmetry of the particles has been assumed for the sake of convenience but as is well understood by those in the field, the particles may be of any size or shape. Therefore, considering a monodisperse system of spherical particles of radius r randomly distributed in a fluid medium, the following considerations apply:

If the volume of the entire system is V_T, and random samples are taken out of the system, the sampling volume being v_s, then the number of particles found in each sample will vary statistically, showing an approximately Gaussian distribution about a mean determined by the individual particle size and the average concentration per unit volume. The half-width of this distribution depends upon the ratio of $\frac{4}{3}\pi r^3$ to v_s. By way of illustration, consider the following three cases.

(*a*) v_s is equal to $\frac{4}{3}\pi r^3$. The number of particles per sample will fluctuate between 0 and 1. Since the average is somewhere between 0 and 1, this represents a large relative fluctuation.

(*b*) v_s is much smaller than $\frac{4}{3}\pi r^3$. Then, the number of particles per sample is always 0, but the frequency with which the sampling volume finds itself within a particle compared to outside a particle is the same as in (*a*) above; with respect to the present application, cases *a* and *b* will yield the same physical result.

(*c*) v_s is much larger than $\frac{4}{3}\pi r^3$. The number of particles per sample will be large, and the relative fluctuation from sample to sample will be small. It is a well-known result of statistical theory that the relative fluctuation (half-width of the Gaussian curve) decreases as the number of particles per sample, n, increases (it is, in fact, proportional to $1/\sqrt{n}$).

Thus, the relative fluctuation in the sampling is small when the sample is large, and increases as the sample volume decreases, reaching a maximum when the sample volume is equal to or smaller than the particle size.

When an irradiation beam is passed through emulsions of liquids in liquids, suspensions of solids in a fluid medium, or aerosols of liquid droplets in air, in accordance with this invention, a beta ray passing through the specimen will encounter both phases in certain proportions, determined principally by the concentration of the mixture. The relative fluctuation discussed above is a function of the ratio of the length of the beta path to the dimensions of the liquid or solid particles encountered by the betas.

The foregoing considerations apply also to dry powders, and to very concentrated suspensions. For example, a perfectly ordered packing of mono-sized spheres would be a rhombohedral arrangement, in which every sphere is in contact with 12 other spheres. The amount of space not occupied by spheres (void space) in such an arrangement can be calculated from simple geometry to be 25.95%. In experimental packings of actual spheres by prolonged shaking, it has been shown that the concentration of voids is 39.5%, which corresponds to an 8-point-of-contact type of packing. Thus, even under the most prolonged shaking, a mono-sized collection of spheres does not adopt a completely ordered arrangement, but instead remains very considerably disordered. It is evident from these facts that the randomness in sampling alluded to above applies even to a well-packed monodisperse dry powder.

Furthermore, Andreasen has shown that the percentage of void space is approximately independent of the particle size for any given degree of shaking or packing (A. H. M. Andreasen, Ingeniørvidenskabelige Skrifter, No. 3, "The Fineness of Solids," Copenhagen, 1939).

In polydisperse systems, the percentage of void space may be as small as 15%, due to small particles filling in the voids between large ones, but the randomness is still as great or greater than in the case of mono-sized dispersions.

The fluctuations in the number of particles per sampling are due to both (1) the existence of an appreciable void space, and (2) the presence of randomness (disorder) in the packing.

For a polydisperse system, the relative fluctuation observed in replicate samplings is composed of the summation of the fluctuations associated with each of the different sizes of particles present.

As indicated hereinbefore, the volume of the specimen that is involved in the measurement in accordance with the present invention, is determined by the area irradiated by the beta beam, the depth of penetration of the betas into the specimen (determined by the energy of the particles and the density of the medium), and the effective viewing aperture of the detector. Hence, there are a number of factors that can be independently adjusted in order to achieve any desired sampling volume.

In utilizing the principles of this invention, these factors are adjusted to give a sampling volume that is of the same order of magnitude as the effective volume of a small number of the particles of the size range of interest in the dispersion under study. Under these fixed conditions, the relative fluctuation in replicate samplings obtained by making slight changes in the position of the detectors relative to the specimen between measurements or by stirring or disturbing the specimen between measurements, will be large. As the sampling volume is increased, the relative fluctuation in replicate measurements due to these particular particles diminishes. Thus, for each predetermined value of the sampling volume, the relative fluctuation is proportional to the cumulative oversize particle concentration, i.e., the total concentration of particles in the size range, from the largest ones present down to a lower limit that is a function of the magnitude of the sampling volume. A series of such measurements made for different sampling volumes, gives the cumulative distribution, which is known as the "characteristic" of the dispersed system (cf. G. Herdan, "Small Particle Statistics," Elsevier Publishing Company, New York, 1953). This characteristic function gives all the information needed for the utilization of particle size distributions in science and industry.

For a particle size analyzer that can be used down to particle sizes as small as the micron range, the radioisotope of choice is tritium, H^3. This is a pure beta emitter, of maximum energy, 18.9 kev. Under conditions of exponential absorption, the half-thickness of water for these betas is approximately 0.5 micron. The "infinite" thick-

ness for back-scattering is proportional to this number, and may be taken as approximately four times the half-thickness. For other absorbers, the "infinite" thickness would be slightly different, but this number can be adopted to give a reliable order of magnitude for the following calculations, which are presented solely for illustrative purposes. If these betas are back-scattered by a specimen, the average beta that reaches the detector would have passed through about 1 micron of the specimen.

(1) If the back-scattered betas are viewed by a detector through a circular opening of about 0.1 mm. diameter, the effective volume of the specimen that is being sampled is small enough that only a few thousand particles of 1 micron diameter could be included, and only about a hundred 3 micron particles, assuming conditions of very close packing of the particles, such as in dry, packed powders; these numbers would be correspondingly smaller for more dilute dispersions.

(2) On the other hand, if the detector viewing pinhole were, e.g. 1 mm. in diameter, the sample could include several hundred thousands of 1 micron particles, but only several dozen 20 micron particles.

The fluctuations observed in the back-scatter intensity in repeated measurements would in Case 1 be a measure of the cumulative percentage of particles 3–4 microns and larger, in Case 2 of ca. 20 microns and larger.

The novel method and apparatus of this invention have wide utility and application.

The industries in which dispersions of fine droplets or solid particles are produced represent an important segment of our national economy. An improvement in the precision with which particle size distributions can be determined will lead to substantial economic gains in these industries. The nature of these needs may be illustrated by the following examples:

(1) In the construction industry, the setting time, rate of pouring, degree of shrinking and cracking, and ultimate tensile strength of Portland cement depend critically upon the particle size distribution. Rapid and precise determination of this parameter are of the greatest importance in the production and utilization of this product.

(2) Certain drugs, such as penicillin and streptomycin, are used in the form of suspensions of the solid in oily or aqueous media which are injected into the body. The ability of these preparations to withstand prolonged storage and to be re-suspended after settling and the rate of absorption of the crystals in the lymphatic fluids are determined by the particle size and size distribution of the crystals.

(3) In the electronics industry, "getters" of zirconium and tantalum are applied to vacuum tube anodes in the form of a suspension by means of a spraying or dipping process. Good adhesion of this suspension to the metal surface is critically dependent upon the particle size distribution.

(4) In the rubber industry, the properties of various commercial rubbers are produced by incorporation of certain proportions of carbon and zinc oxide powders as fillers. The size distributions of the particles of these fillers are of primary importance in determining the success of these operations.

Other industries in which particle size distributions are of similar primary importance include: abrasives, ceramic materials, dusts (such as in milling and storage facilities), dyes, cosmetic emulsions, photographic emulsions, salves and ointments, fertilizers, fuels, metal powders (as in powder metallurgy), muds, ores, pigments for paints, plastics, soils, foods, and explosives.

The invention in its broader aspects is not limited to the specific steps, methods, combinations and improvements described but departures may be made therefrom within the scope of the accompanying claims without departing from the principles of the invention and without sacrificing its chief advantages.

What is claimed is:

1. A particle size analyzer for use in obtaining data relating to particle size and particle size distribution with respect to a composition having an imperfectly ordered arrangement of particles, comprising means for applying to said composition radiant energy which reacts substantially simultaneously with a plurality of said particles and which is sensitive to the several phases of the composition; means for controlling the degree of irradiation by said radiant energy, means for adjusting the dimension of a sample region of said composition to a magnitude which is of the same order of magnitude as the dimension of a small number of certain of said particles, and means for measuring the reaction of said sample region to said radiant energy to provide data with respect to said sample.

2. A particle size analyzer according to claim 1, wherein the means for providing said radiant energy is a radioisotope.

3. A particle size analyzer according to claim 1, wherein the reaction measuring means include detector means for measuring rays of said radiant energy affected by said composition and said adjusting means comprise aperture means for controlling the effective dimensions of said sample, the reaction of which is measured by said detector.

4. A particle size analyzer according to claim 1, wherein said reaction measuring means comprise means for measuring back-scattering by the sample under consideration.

5. A particle size analyzer for use in obtaining data relating to particle size and particle size distribution in a composition having an imperfectly ordered arrangement of particles comprising means for irradiating substantially simultaneously a plurality of particles in said composition with radiant energy which is sensitive to the phases of said composition, a plurality of detecting means responsive to the reaction of said radiant energy with said particles, sample defining means corresponding with each of said detecting means for rendering said plurality of detecting means responsive respectively to the reaction of a plurality of equi-dimensional but differently located sample regions of said composition, measuring means differentially responsive to said detecting means for measuring fluctuations between the outputs of said detecting means and means included in said sample defining means for limiting the dimensions of said sample regions to values where the percentage fluctuations vary as a function of said dimensions.

6. Apparatus according to claim 5 including means responsive to the absolute output of at least one of said detecting means whereby in conjunction with said differential measuring means, the percentage value of said fluctuations may be determined.

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CERTIFICATE OF CORRECTION

Patent No. 3,098,931 July 23, 1963

Seymour Z. Lewin

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 3, Table I, first column, line 9 thereof, for "Y^{99}" read -- Y^{90} --; column 5, line 17, for "meachanical" read -- mechanical --.

Signed and sealed this 31st day of March 1964.

(SEAL)
Attest:
ERNEST W. SWIDER

Attesting Officer

EDWARD J. BRENNER

Commissioner of Patents