

FINE PARTICLES IN THE COSMETIC INDUSTRY

By H. W. HIBBOTT, M.Sc., Ph.D., A.R.I.C.

A lecture delivered before the Society on Friday, January 4th, 1957

IN APPROACHING this subject the first thing of note is the immense amount of work that has been done particularly in the last thirty years. Apart from academic research, much work has been carried out by many industrial organisations, so that literature on the subject is very widely dispersed through scientific journals in this country, America and Europe. The main difficulty in preparing this paper has been rather what to leave out than what to put in.

The information on particulate matter desired by one industry will differ appreciably from that of another, depending on the use for which the material is required. For instance, in cement the setting properties depend on the total surface of the particles, and this feature is important also for powdered fuels and explosives. On the other hand, many industries are interested in particle size range. In glass polishing the interest is in the very small fraction at the coarse end of the range of particle size, for in this case the incidence of one comparatively large particle in ten million can cause great trouble by deeper scoring of the glass surface. In the pharmaceutical industry there is interest in the particle size of some medicaments, for where such products are ingested only slowly the particle size will control the rate of assimilation and therefore dictate the time of effectiveness. In the cosmetic industry the more important needs are performance and efficiency of grinding processes; powder separation, transmission and collection; control of particle size in finished products. In general, for cosmetic work particle sizes should be less than about twenty-five microns because solid particles above this size may be recognised by sight and touch as single particles. Moreover, for dry applications to the skin the finer the particle size of a given material the more adherent it is to the skin surface.

In considering the raw materials for this industry, naturally occurring minerals must be ground in some way; manufactured materials may be produced chemically in a fine enough state of sub-division or may require to be ground after manufacture. The fineness of some materials may be dictated by the needs of other large industrial users. Other materials may be produced specifically for the cosmetic industry.

The range of particle size of materials used in this industry are of the following order :

Talc	150	—	5 microns
Kaolin	35	—	1 micron or less
Pptd. chalk	10	—	below 1 micron
Magnesium carbonate	5	—	below 1 micron
Metal soaps	50	—	1 micron
Zinc oxide	5	—	0.25 microns
Titanium oxide	0.5	—	0.1 micron
Natural iron oxide colours	50	—	5 microns
Synthetic iron oxide colours	25	—	2 microns
Lakes and pigments	10	—	below 1 micron

Processing of such materials involves mixing and grinding by wet or dry methods. For wet grinding methods, the triple roller mill and high-speed cone mill are most used. In both cases the grinding face clearances of the machines are controllable down to about 30 microns although usually grinding operations are carried on with gaps much wider than this. Perhaps of more interest for the purposes of this paper are the dry grinding processes. The types of mill most favoured are the high-speed beater mills and to a small extent the vapour-jet pulveriser which are continuous feed processes, and ball mills which are batch processes. For a given material each type of mill has its own optimum efficiency in terms of increase of surface for a given energy input. Again each type of machine will have a best working range from a certain size of fed material to a certain size of ground product. These variations are connected with the friability of the material and design of machine. In high-speed beater mills the variables are feed rate, speed and shape of hammers and design features such as incorporated sieves and air-classifying systems. In ball mills the performance will depend on the shape, size and load of balls, the load of material and the number and rate of revolutions of the machine. Wherever cushioning of coarse particles in a bed of fine particles can occur in a grinding process there will be loss of grinding effect and energy will be wasted in heating up the product.

For the continuous operating machines close attention should be paid to keeping the feed rate as constant as possible. As will be appreciated from the general size range of cosmetic raw materials much of the capacity of grinding machines will be devoted to breaking up agglomerates of individually fine particles rather than primary comminution of oversize particles. In other words, such machines are operating largely as mixers but the energy input per given weight of material is appreciably greater than in conventional mixing machinery.

In considering methods of particle size measurement it will become obvious, and needs to be kept in mind constantly, that adequate sampling of the material is of prime importance. Theory and practice of sampling is a large subject in itself and has a very extensive bibliography. One should be reasonably sure that the sample to be examined is representative of the bulk.

SIEVES

To come now to particle size measurement, the coarser fractions are dealt with by means of sieves. Here again the theory and technique of sieving has been the subject of a great amount of work. As most cosmetic materials are in the sub-sieve range I do not wish to consider sieves further here except for one or two comments. Their use for us will be confined to the natural minerals and to cases where accidental oversize particles are encountered. The practical lower limit of particle size measurement obtainable by sieving is 40–50 microns. It is perhaps not too trite to point out that sieves, particularly the finer ones, are high-precision instruments and should be treated as such. The mesh should be checked occasionally with a measuring lens. There is no limit to the amount of sample which may be examined in usually 10–50 gm. batches.

MICROSCOPE

The optical microscope has been much used for particle size determination in the sub-sieve range and some authorities still consider it the best. However, it is a very tedious time-consuming method and the amount of sample examined is extremely small. When it is realised that a 40-micron particle of, say, talc weighs about 10^{-7} gms. and a 2-micron particle about 10^{-11} gms., a count of 10,000 particles in this range may not amount to more than one-tenth of a milligram, and the reliability of sampling becomes of great importance. Much depends on the operator and the preparation of slides.

ELUTRIATION AND SEDIMENTATION

Many designs of apparatus have been based on the principle of vertical movement of solid particles in a fluid medium. Elutriation involves movement of particles in a rising column of fluid, usually water or air, and sedimentation the downward movement of the particles in a stationary column of liquid.

The terminal velocity of fall v of a particle depends on the "diameter" d and density σ of the particle, the density ρ and viscosity η of the fluid, and on gravity g . The relationship is expressed by Stokes law (c.g.s. units),

$$v = \frac{d^2(\sigma - \rho)g}{18\eta}$$

Dealing first with elutriation in which separation of the powder is achieved by suspension in a rising column of fluid an upward speed of fluid is fixed according to the desired particle size cut. Particles coarser than this size will fall, and particles finer than this will rise to be collected and weighed. A series of such cuts must be made to give a measure of particle size range. Multiple instruments have been designed having a series of columns of successively larger diameters to give three or more fractionations in one operation. Examples of types :

Single cut	Gonell Air Elutriator.
Double cut	Andreasen Air Elutriator. Andrews Liquid Elutriator.
Multiple cut	Haultain Infrsizer (Air).

The size of sample used in such instruments is 10–50 gms. depending on density of particle, and the method is useful over the range of 10–50 microns. The main difficulty in such instruments is to maintain the fluid stream steady and even over the cross-section of the column. Further, and particularly with air elutriators, dispersion of the powder as single particles is almost impossible with some powders. By the same token the rising particles will adhere strongly to the surface of the column and re-agglomerate. Some form of vibration of the apparatus is often required. The time necessary for a determination by this method is very variable—from a few hours to a few days, depending on the nature and the particle range of the powder. Nevertheless it is very useful in some circumstances, particularly when close particle-range fractions are required for further examination.

Looking back to the Stokes equation, it will be seen that increase of g would reduce the time of a determination. Consequently several methods have been devised using centrifuges, particularly in liquid media. A centrifugal method of the air elutriation type has recently become available. The material is fed from the central point of a rotating chamber against a spiral air flow and the powder thereby separated into two fractions above and below the required particle size cut. The particle size cut is controlled by the speed of the rotor, which must be kept constant for each size limit, and by the spacing plate at the air induction point. The feed is of the vibrator type, closely controlled to a rate of 1–2 gm. per minute. When the finest fraction has been removed the residue is returned to the feeder and the whole repeated at a different setting. The instrument will deal with 10–40 gm. sample.

Sedimentation methods may be exemplified by the Andreasen pipette. A weighed amount of powder is suspended in a column of volume about 600 millilitres and height about 25 cm. The time of fall through a height of 20 cm. is calculated from Stokes Law for a series of particle sizes. At such times after the beginning of the operation a 10 ml. sample of the suspension is withdrawn from the level at 20 cm. below the top surface of the column. This is transferred to a dish, the suspension evaporated to dryness and the residue weighed. This residue is the weight fraction of the sample which is less than the particle size which had been used to calculate that particular period of settling. In this method 7–20 gm. of sample may be used, corresponding to 1 per cent by volume of the suspension.

Many refinements of the sedimentation method have been attempted. One such incorporates a scale pan in the bottom of the suspension and gives a continuous register of the amount of deposition.

Other devices have been based on the fact that a suspension has effectively a density somewhat higher than the pure fluid, and which can be measured by means of a hydrometer. As the suspension settles out its density falls off and so gives a corresponding change in the hydrometer reading. Unfortunately, the hydrometer has to be removed from the suspension between readings to avoid deposition of particles on the shoulder of the bulb. Such disturbances of the suspension are not desirable. There is also the difficulty of surface tension effects where the hydrometer breaks the surface. A better alternative is the use of small divers in the suspension. Several divers of different densities are required. They are streamlined in shape and the falling particles do not settle on them. As the suspensions are usually opaque the divers may be fitted with a ferrous core so that they may be brought to the side of the column by means of a magnet. A later refinement of this has been detection electrically of the position of the divers (with permalloy cores) by means of a thin search ring around the outside of the column.

Manometric measurements of changing density of a suspension have been used. Two tubes fitted with pure liquid are immersed in the suspension at different levels. The slight difference in heights of the manometers is proportional to the mean difference in density between the two levels. The manometric readings are made with a travelling microscope.

Probably the most attractive modification of the simple Andreasen type is the photo-extinction method. Here a narrow beam of light is directed through the suspension at a set level below the surface of the suspension and the fraction of the light which passes through is measured by a photocell system. As the particles settle out less light is obstructed and the increasing light intensity picked up by the photocell gives a measure of the particle range. This method has the great virtue that the suspension is not disturbed during the course of the determination. It can be made more rapid than the pipette method by moving the light beam to higher levels for finer particles. Much experimental work has been done on this method since it was first examined some twenty years ago. The theory of the method is very complex. Its range is about 25 microns—1 micron. The amount of sample examined is about 0.01 gm. Difficulties in interpretation occur on account of light scattering by the particles and the transparency of some materials at low particle sizes.

PERMEABILITY METHODS

We have considered the movement of particles against a moving stream of fluid (elutriation), and the movement of particles in a standing column of fluid (sedimentation). The so-called permeability methods first investigated by Carman make use of movement of fluid through a standing column of

particles. As air is forced through a bed of powder the viscous drag, which is related to the surface area of the particles, causes a differential pressure to be set up across the bed of particles. The difference in pressure is correlated with the total surface of the particles forming the bed and so gives a single figure of specific surface (cms. per gramme). It is very attractive to be able to express the size of a powder as a single figure but for many purposes it does not give enough information. Since the method was first devised twenty years ago, it has been developed into a very simple apparatus easy to use even in unskilled hands. It gives repeatable results for given materials and by carefully standardised forms of procedure has become a standard method in some industries where the particle range of powders is small; for example, the cement industry. Despite much work on the theory of the process there is uncertainty about the absolute values for particle surface obtained by this method. This difficulty turns on what is meant by surface. Some surfaces are very much more fissured than others. There is some difficulty in assessing if the method applies to the gross surface or includes also some or all of the finer structure of the surface.

OTHER METHODS

Attempts have been made to measure the surface of a bed of powder by gas adsorption by which it is possible to differentiate between the outer surface and the fine structure surface. The sample to be treated is out-gassed to a pressure of 10^{-4} m.m., and the adsorbant gas is then admitted to the powder from a gas burette until saturated. In the same way solutes may be adsorbed from solutions by particles to give a measure of surface area. The powder is immersed in a suitable dye solution of known concentration, stirred until a state of equilibrium is reached, then the strength of the residual dye solution determined by suitable titration. The relation between amount adsorbed and the equilibrium concentration is complex but has been worked out to express the monolayer capacity and hence the specific surface of the powder. This demands a knowledge of the molecular dimensions and orientation of the adsorbate, and this is rarely known with accuracy. Since dyestuff molecules are comparatively large they will not penetrate the finer pores. Iodine has a much smaller molecule and so can penetrate further than a dye molecule. It is found, in fact, that estimation of surface by means of iodine solution will give higher results than with a dye solution.

A further method of this type is measurement of heat of wetting which will be proportional to the surface area of the powder. Here again the sample must be freed from any adhering gases by high vacuum before being introduced into the wetting liquid in a calorimeter.

Of these three methods the dyeing technique is very simple to perform. The gas adsorption method will yield absolute values, the other two methods somewhat more relative values.

One method of particle size measurement which I have not mentioned so far is the electron microscope. This, of course, has widened greatly the scope for examination of extremely fine powders. It goes beyond the magnifying power of the optical microscope to give resolution of particles of 0.01 micron and less. At the same time the amount of sample examined is proportionately lower. Its great scope would seem to lie in revealing fine particle structure which will help to explain some of the anomalies observed in the more statistical methods.

ANDREASEN METHOD

Having described some of the methods of particle size determination together with their attendant advantages and shortcomings you might expect me to tell you which is the best. This is impossible, of course, because much depends on the purpose for which the information is needed. For this industry I would say that possibly the Andreasen pipette supported by a good microscope is the most versatile instrument. It is simple to use, and cheap. It can be used over a wide range of materials and many suspending fluids may be used. A determination may be completed in a day and will occupy only two hours of an operator's time. The sample examined is 7-15 gm.

In view of this I would like to give a little more detail of the sedimentation method. The flow of a particle in a liquid has been very extensively studied. The type of flow has been described as streamline gradually changing to turbulent as the speed of the particle increases. For streamline flow the speed of fall is proportional to the square of the diameter of the particle. As the speed of the particle increases eddies begin to develop around the particle and to impede its flow. In fully turbulent conditions the speed of fall becomes proportional to the square root of the diameter. In sedimentation work care should be taken to keep the motion in the streamline range.

The form of flow can be calculated from the known properties of the suspension by the magnitude of the Reynolds Number

$$R_e = \frac{\text{Velocity of particle} \times \text{diameter}}{\text{Kinematic viscosity of the liquid}}$$

For values of this expression up to 0.2 the motion is streamline. For fully turbulent conditions the value is over 700. For most materials up to 60 microns and density up to 4 the movement is essentially streamline in water, and the Stokes equation involving d^2 may be used.

The interaction between the particles themselves is always a problem. In the sub-sieve range for a 1 per cent suspension by volume the average distance apart is of the order of four or five diameters. Andreasen considered this sufficient clearance to allow the particles to fall freely. Some other authorities consider that the free space around the particle should be

about fifteen diameters. There is no doubt that from this point of view the more dilute the suspension the better. However, 1 per cent concentration, whilst not ideal, does not give rise to errors approaching the overall error inherent in the method. The 1 per cent concentration is about the minimum to allow of reasonable accuracy in the weighing of the sampled fractions. The overall error in determinations of particle size by the Andreasen method has been estimated as ± 0.5 per cent. This may be true for an expert operator. The error may vary somewhat with the nature of the material. I would put the figure for a good operator as ± 1.5 per cent.

One important feature of the Andreasen method which must be stressed is the necessity for close temperature control during the determination. Slight changes of temperature at the outside wall of a column will set up convection currents which will completely invalidate the method for the finer particles. Andreasen points out that convection hazards are less troublesome with more concentrated suspensions and considers this another point in favour of using a suspension of initial concentration as high as 1 per cent.

It has been considered that the zone of suction around the immersed tip of the pipette is far too widespread. It should, of course, be kept to a minimum by very careful steady suction at the time of sampling the suspension. Even so, the withdrawal of the sample should not take longer than 15 seconds for water, and a little longer for more viscous fluids. Two other small points, but important ones: the column should be vertical and the determination carried out in a place free from vibrations.

PARTICLE SIZE

Having said so much of the measurement of particle size we come to the problem of what is the size of a particle? As far as the microscope is concerned a particle on a slide will tend to rest with its smallest dimension in the vertical plane. The particle is normally viewed in silhouette so that one sees the projected area. The usual method is to match this area to a sphere of the same area or to a circumscribing rectangle, and the particle size is described in terms of such references. Where many particles have to be measured the dimension termed a statistical diameter is sometimes used. This is the length of the line bisecting the projected area of the particle as it lies on the slide, and read off in the same direction for all particles measured.

The particle size may also be described as the diameter of a sphere of the same surface area as the particle or again as the diameter of a sphere of volume (or weight) equal to that of the particle. In the case of sedimentation methods, Stokes Law, of course, refers to spheres. Here the usual description of particle size is the diameter of a sphere of the same density

as the particle which falls at the same speed as the particle. (This is the "diameter" used in Stokes Law above.) Correlation of these different descriptions of particle size have been made in some cases. They involve the establishment of shape factors for the particles. For instance, the total surfaces of stones have been measured by wax dipping and their volumes by displacement in a fluid. In this way correlation may be obtained between an equivalent surface diameter and an equivalent volume diameter. This ratio may be considered to be constant for a given material in that it tends to fracture in a set way. For large particles of the size of pebbles the ratio does hold over quite a range of size. But whether this can be extended down to particles of 20 microns or less is debatable. Uneven particles have been classified to simulate a small number of geometrical shapes and this offers some means of assessing shape factors.

AGGLOMERATION AND DISPERSION

Particulate matter, particularly of 5 microns and finer, when placed in a liquid medium, may coalesce into agglomerates of particles. Where this occurs in sedimentation methods a clump of particles will behave as if it were one large particle, giving completely erroneous results. Checks should be made that the material does not coalesce in the liquid selected. Parallel trials should be made using a series of liquids and the one settling most slowly taken as free from agglomeration. Many effective dispersing agents have been used to combat agglomeration and references are dotted about through the literature. They seem to be specific for some materials. There does not seem to have been any systematic investigation of this phenomenon. It would seem that at least two factors are involved—wetting of the particles and electrostatic charges. Perhaps in some cases a wetting agent is also a good dispersing agent. There is no universal dispersing agent although sodium hexametaphosphate and pyrophosphate (0.001 to 0.01 per cent weight/volume of suspension) are useful in many instances. Other dispersing agents in common use are such compounds as sodium silicate, potassium citrate, sodium oxalate. Failing these there are many suitable organic liquids which are listed in the literature for specific materials.

Some variation in dispersibility may occur in the case of natural minerals which may contain small, variable amounts of soluble salt occlusions, and in materials which are themselves slightly soluble in the liquid selected.

In conclusion, I would say that the work on particle size analysis has been increasing over the past ten years, as indicated by the symposia and conferences organised on the subject, notably in this country by Society of Chemical Industry, Institute of Mines and Metallurgy, and most recently by the Institute of Physics. The latter conference produced some clarifying concepts of the relative motion of particles and fluids, on light scattering by particles and on particle shapes. It was also shown that the tiring work

of microscope technique of counting and measuring fine particles could now be handed over to electronic scanning instruments.

For anyone wishing to pursue this subject further the following publications should be consulted. They all carry extensive references to the literature on the subject, both academic and applied.

Heywood, *Trans. Institution Mech. Engineers, London* (1933).

Heywood, *ibid.* (1938).

Am. Soc. for Testing Materials. Symposium on Particle Size Determination (1941).

B.C.U.R.A. and B.C.O.R.A., London, Report on Determination of Particle Size (1944).

Inst. Chem. Engineers, London. Symposium on Particle Size Analysis (1947).

Dalla Valle, *Micromeritics* (1948).

Brit. Journal Applied Physics, Suppl. 3 (1954).

Finally, I must thank Dr. H. Heywood of Imperial Institute, London, for slides used to illustrate this lecture, and Miss L. P. Torry, a fellow member, for help in preparing the paper.

Erratum. In the article on "Smell-Threshold Concentration," by A. W. Middleton, B.Sc., Ph.D., F.R.I.C., which appeared in Volume VIII, No. 1, of the *Journal of the Society of Cosmetic Chemists*, the word "basis" appearing in line 3, paragraph 4, page 41, should read "hairs."