

# THE PARTICLE SIZE DISTRIBUTION OF MARBLE ON WET BALL MILLING

EFFECT OF THE SOLID : LIQUID RATIO

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An investigation has been made of a wet ball milling procedure which depends on the apparent viscosity of the charge increasing during the operation until the balls are held by the charge, and circulate with the mill. By varying the solid : liquid ratio of the charges the mean particle size of the product was changed, and shown to be a linear function of the proportion of solid in the charge. The effect of changing the ball size is discussed.

THE critical speed  $N_c$  of a ball mill is the rotational velocity at which the balls cease to grind, and are carried around with the mill by centrifugal force. In wet milling the viscosity of the liquid affects the critical speed, since it impedes the fall of the balls, and brings about critical conditions below those predicted by the generally accepted formula

$$N_c = KD^{-1/2}$$

where  $D$  is the diameter of the mill, and  $K$  is a constant depending on the units in which  $D$  is measured. As the particle size of the charge is reduced, the apparent viscosity of the suspension increases, so that critical conditions can result after milling for a given time, even though the rotational velocity of the mill was below critical at the beginning of the operation. Coghill and De Vaney (1937) have suggested this sequence as the cause of an observed fall in the rate of comminution with time.

Frequently it is important that a pharmaceutical material be presented within a narrow particle size range. Thus it was considered that a study of the behaviour described above might reveal a self limiting method whereby milling would stop to give a pre-determined and reproducible particle size range.

## EXPERIMENTAL AND RESULTS

### *Materials*

Marble chips of chemical reagent quality were ground in an end runner mill, and material which passed a number 10 but not a number 22 sieve was used for milling. A saturated aqueous solution of calcium carbonate was used as the liquid phase in the ball millings, and as a diluent in the sampling procedure; this was prepared from the fines. To obtain a satisfactory medium for the determination of particle size distribution after milling, Dispersol T (I.C.I. Ltd.) and Antifoam Emulsion A (Midland Silicones) were used.

### *Milling Procedure*

Milling was carried out in a 16 oz. cylindrical glass pot of diameter 2.5 in. using stainless steel balls, which together with the voids filled half of the pot. The same weight of balls was used in every experiment, and the total charge of marble and liquid was maintained at 200 g. This together with the balls occupied 65 per cent of the volume of the pot. A constant velocity of 140 r.p.m. was used throughout and milling was continued until every ball was circulating with the mill.

A series of millings of marble chips (10/22 mesh) were made in a saturated aqueous solution of calcium carbonate using  $\frac{3}{8}$  in. balls, and varying the solid content of the charge from 0.375 to 0.625. Experiments were confined within these values since charges containing less than 0.375 of solid took over a week to reach limiting conditions, while solids in excess of 0.625 were not reduced completely and yielded a proportion of unmilled material.

In repeating the procedure with  $\frac{1}{2}$  in. balls, their greater mass enabled them to mill charges containing a larger proportion of solid. The range used was from 0.3 to 0.7. With the  $\frac{1}{4}$  in. balls, the upper limit of solid was 0.425 so that weaker charges had to be examined. Charges containing less than 0.25 of solid took more than five days to reach limiting conditions, consequently 0.25 was used as the lower limit.

### *Sampling*

The sampling procedure was a development of a technique by Ellis (1953). The balls were strained off through a coarse sieve, and the milled material suspended in 1 litre of saturated calcium carbonate solution containing 1 per cent Dispersol T, to stop aggregation of the particles, and 1 part per million of Antifoam Emulsion A. The suspension was transferred to a beaker and stirred mechanically at a speed such that the solid was uniformly suspended, and no air was introduced. After 10 min. 0.1 ml. was withdrawn (the pipette being gradually raised in the beaker during the operation) and adjusted to 100 ml. After shaking for a few min. one drop was transferred to a Thoma haemocytometer slide and the particles counted in the usual manner. First double image diameters of the particles, as described by Timbrell (1962) were measured using a Timbrell Double Image Micrometer and Particle Size Analyser. This instrument and procedure have been described elsewhere by Barnett and Timbrell (1962).

To show that there was no preferred orientation of the particles, the first double image diameters of 1,000 particles were measured, then the field moved through 90 degrees and the new diameters of the same particles measured. There was no significant difference between the two sets of measurements.

It was found adequate to measure 1,500 particles and to place these in size groups since no significant difference in distribution or average diameter was observed in the histograms derived from a batch of 1,500 particles or from one of 3,000 particles.

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For each experiment six samples were taken, and 250 particles measured in each sample. The size distributions of the particles obtained with  $\frac{3}{8}$  in. balls are shown in Table I.

TABLE I  
VARIATIONS IN PARTICLE SIZE DISTRIBUTION WITH CHANGES OF WEIGHT RATIO OF SOLID IN CHARGE USING  $\frac{3}{8}$  IN. STAINLESS STEEL BALLS

Size Group ( $\mu$ )	Number of particles in each size group for the following values of weight of solid					
	weight of solid and liquid					
	0.375	0.400	0.425	0.500	0.575	0.625
1-2	43	5	15	19	—	—
2-3	815	405	647	237	201	157
3-4	446	836	582	723	942	835
4-5	127	169	130	236	172	234
5-6	31	29	50	114	51	82
6-7	9	15	23	61	56	43
8-10	16	15	22	57	64	93
10-15	8	11	13	28	22	33
15-25	3	7	10	10	3	14
25-50	0	0	0	0	8	8

### DISCUSSION

The most obvious parameter of particle size distribution with which to compare the results would appear to be the arithmetic mean of all the measurements, that is, the mean diameter  $d_{av} = \frac{\sum nd}{\sum n}$ . However,

since the fine particles are more numerous than the coarse particles, this would represent only a small portion of the total weight of the mass.

The mean volume diameter,  $d_v = \sqrt[3]{\frac{\sum nd^3}{\sum n}}$ , and the weight mean

diameter  $d_w = \frac{\sum nd^4}{\sum nd^3}$  are more representative of the bulk of the mass.

The mean volume diameter has been defined by Dallavalle (1948) as the diameter whose corresponding volume divided into the total volume, gives the total number of particles. Perrott and Kinney (1923) have defined the weight mean diameter as the diameter  $d_w$ , such that half the weight of the sample consists of particles of diameter  $d_w$  or less, and half of the particles of diameter  $d_w$  or more. The two means coincide only in normal distributions, and the difference between them is a measure of the degree of skew.

The variations of the three means described above with weight fraction of solid in the charge are plotted in Fig. 1. and in each case a linear relationship obtains. Examination of Table I shows that these changes are not due to a shift of the maximum from the 2 to 4  $\mu$  region, but to an increase in the number of particles occurring in the higher size groups. This is confirmed from Fig. 1 since the difference between  $d_v$  and  $d_w$  increases with weight fraction of solid, indicating an increase in skew in the distribution curves.

Both the volume and the mass of the balls are altered by changing their size, and these affect the final particle size in opposite ways. It is well established that with smaller balls there are more points of contact, and the milling is more efficient. In the procedure described, however, the heavier the balls, the longer will they resist the retention by the charge, and once again a finer product will result. Fig. 2 shows the variation of weight mean diameter with weight fraction of solid for the three ball sizes, and shows there is no correlation between ball size, and the particle size of the product. It is suggested that the effects of mass and volume,

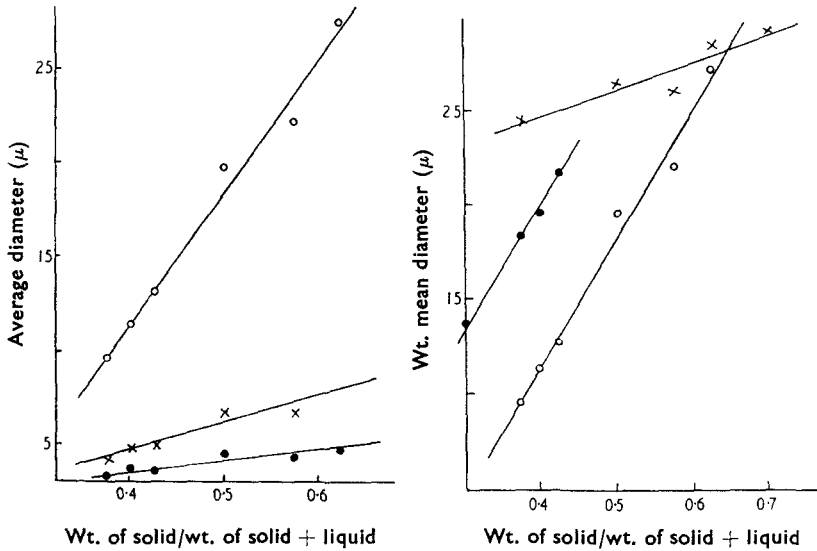


FIG. 1. Effect of solid content of charge on particle size of product

- Mean diameter ( $d_{av}$ )
- $\times$  Mean volume diameter ( $d_v$ )
- Weight mean diameter ( $d_w$ )

FIG. 2. Effect of ball size on weight mean diameters.

- $\frac{1}{4}$  in.
- $\frac{3}{8}$  in.
- $\times$   $\frac{1}{2}$  in.

working against each other are responsible for this lack of correlation, so that with the  $\frac{1}{2}$  in. balls the disadvantage of having a larger volume than the  $\frac{3}{8}$  in. balls is greater than the advantage of their heavier mass, while with the  $\frac{1}{4}$  in. balls the weight disadvantage exceeds the advantage gained from having a smaller volume.

It is apparent from the results that the average particle size of the milled product can be influenced by using the process that has been described. Further, since the relationship between average size and weight fraction of solid is linear, then if two millings be carried out with different solid:liquid ratios, all other conditions remaining constant, the mean particle size produced by any other ratio can be predicted. Alternatively a solid:liquid ratio necessary for a required average particle size may be calculated.

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### DISCUSSION

The paper was presented by MR. BARNETT. The following points were made in the discussion.

Marble was selected for its insolubility in water. The criteria for selecting the weight of balls and charge were the half-way filling of the mill with the balls, which were then adjusted to a specific weight, and sufficient charge, also adjusted to a specific weight, to fill the void spaces and to cover the balls. The endpoint at which the balls ceased to move was sharp. Errors within and between observers making the particle analysis were low and smaller than usual in microscopical analysis.