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Research Papers

MILLING KINETICS OF GRANULES

J.T. CARSTENSEN, F. PUISIEUX, A. MEHTA * and MICHAEL A. ZOGLIO *

Universite de Paris-Sud, Laboratoires de Pharmacie Galénique, 92290 Châtenay-Malabry (France) and
** Merrell-National Laboratories, Cincinnati, Ohio 45215 (U.S.A.)*

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SUMMARY

It is shown that ball milling of granulations gives rise to particle size diminution, the extent of which can be explained by Kick's law. It is shown that of w grams of granulation of original diameter d_a the amount (w_b) of finer material produced (d_b) relates to time t by the equation:

$$\ln[(w_a/w) + (w_b d_b/\{wd_a\})] = -Kt$$

where K is a granulation-dependent constant; d_b is time independent for a particular granulation, but depends on the amount of binder used and hence the equation can be used to evaluate optimum amounts of binder.

INTRODUCTION

When material is ball milled, the amount of material of original size will decrease with time. In most situations, if w grams are milled the amount of material of the original diameter, d′, at time t will be w_a, such that

$$\ln w_a = -k't \tag{1}$$

i.e. first order (Austin, 1971/1972). Deviations from this have been reported (Austin et al., 1976) and explained by kinetics of the type

$$A \rightarrow A^* \rightarrow B$$

where A* is a particle of A which has been rendered softer than it originally was (but still is of side d′). In these situations plots of ln w_a versus time will have curvature away from the abscissa.

In contrast to this, ball milling of granules made by wet granulation procedures frequently give ln w_a versus time plots with curvature towards the abscissa. It is the intent of this article to propose an explanation for this.

METHODS

Granulations were made in a planetary mixer by mixing 1.75 kg of lactose U.S.P. of particle size 20 μm with 0.75 kg of cornstarch U.S.P. and granulating this with a solution of x grams of polyvinylpyrrolidone in (300 – x) ml of isopropanol. x was varied from 25 to 100 g in increments of 12.5 g. In one case the polyvinylpyrrolidone (x = 40) was added to the lactose and cornstarch, mixed, and the granulation performed with 260 ml of isopropanol.

A formula was also made where the lactose and cornstarch was granulated with 100 ml of a 10% solution of gelatin U.S.P. The granulations were dried at 60°C and sieved, and the 14/20 and 20/40 U.S. Standard Sieve mesh fractions retained. The crushing strength of some of the 14/20 mesh fractions were obtained by the method of Harwood and Pilpel (1968) as described by Zoglio et al. (1976).

Sixty grams of 14/20 mesh granules were milled in a ball mill of inside diameter 6.7 cm and length 13.5 cm. One hundred steel balls with a diameter of 0.53 cm each weighing 0.993 g were used and the mill operated at a speed of 120 rotations per minute. Material ball milled for t min was subjected to sieve analysis through a 20 mesh sieve. The amount of material, w_a g, remaining on the 20 mesh sieve was recorded. In several cases the $w_b = 60 - w_a$ g of material passing the 20 mesh sieve was subjected to full sieve analysis. The same procedure was carried out for several of the granulations with the 20/40 mesh sieve fraction, in which case the value of w_a was obtained by sieving through a 40 mesh screen.

RESULTS

The distribution of the undersize material was log-normal, as predicted elsewhere (Steiner et al., 1974; Carstensen and Patel, 1974). Table 1 shows mean particle diameter, d_b (in μm) of the fine fraction, and it is apparent that d_b is time independent in the time intervals studied (0–10 min). The ln w_a versus time curves have the shapes shown in Fig. 1.

DISCUSSION

Kick's law (Parrott, 1970) states that if a material of particle size (diameter) d′ is milled and the milled material has a particle size (diameter) of d″, then the energy expended is given by:

$$E = C \ln(d'/d'') \tag{2}$$

The original diamter in this study is d_a μm, the mean sieve size of a 14/20 U.S. Standard Sieve fraction (or 20/40 mesh fraction when this was milled), and this may be substituted for d′ in Eqn. 2. At time t when there are w_b g of diameter d_b and w_a g of diameter d_a

TABLE 1

PARTICLE STATISTICS AND HARDNESS OF GRANULATIONS MADE FROM POLYVINYLPYRROLIDONE AND GELATIN

x (g)	Original mesh	Mean diameter (μm) of fines at various t					d_b (Expt)[a] (μm)	db (It) (μm)	d_a (μm)	Crushing strength[b] (g/mg)
		2 min	4 min	6 min	8 min	10 min				
25	14/20							250		
37.5	14/20	398	382	360	368		376 ± 6	360	1135	135
50	14/20							450		
62.5	14/20	502	513	515	511	491	507 ± 10	520	1135	245
75	14/20							500		
87.5	14/20	518	538	528	528	525	527 ± 7	530	1135	305
100	14/20							550		
Gelatin	14/20	755	566	515	505	496	524 ± 10	510	1135	600
37.5	20/40	199	201	198	190		194 ± 5	190	638	
62.5	20/40	222	223	227	228	229	226 ± 10	235	638	
87.5	20/40	262	244	245	240	245	247 ± 4	260	638	
Gelatin	20/40	287	276	257	266	272	271 ± 8	265	638	

[a] Data which have been pooled from all the time points, showing 95% confidence limits.
[b] Harwood-Pilpel hardnesses.

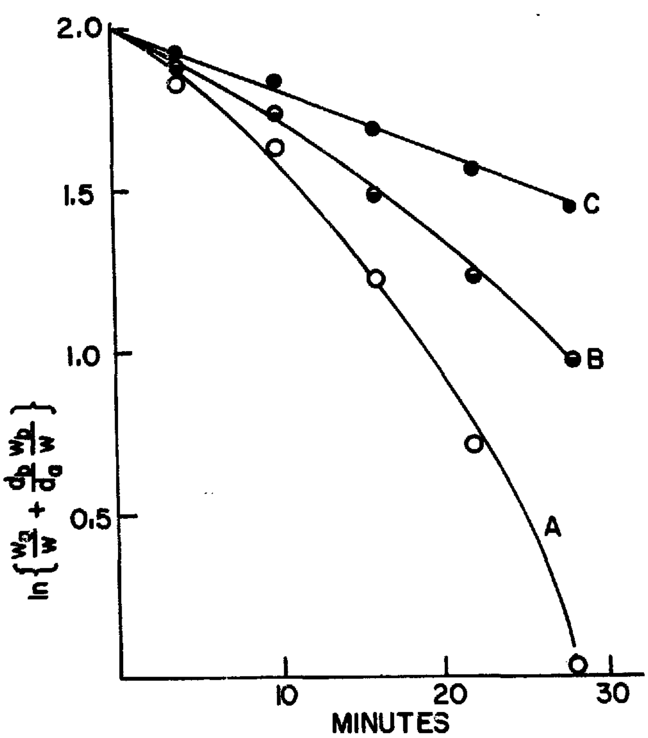

Fig. 1. Iterative plotting according to Eqn. 5 of a granulation made according to the granulation (x = 40) where the polyvinylpyrrolidone had been added dry rather than in isopropanolic solution). Curve A: data as is; curve B: d_b/d_a 0.25; curve C: d_b/d_a 0.5.

the mean particle diameter of the powder population is:

$$d'' = (w_a d_a + w_b d_b)/w \quad (3)$$

The energy input is proportional to the length of time of milling, i.e.:

$$E = qt \quad (4)$$

Combining Eqns. 2–4 then gives:

$$y = \ln\left[\frac{w_a}{w} + \frac{w_b d_b}{w d_a}\right] = -Kt \quad (5)$$

where

$$K = q/C \quad (6)$$

d_b can be found as the diameter which linearizes y with time. This is demonstrated in Fig. 1. That this method indeed leads to reasonable figures is demonstrated in Fig. 2 where d_b values found by iteration, denoted $d_b(\mathrm{It})$, are plotted versus d_b values ($d_b(\mathrm{Expt})$)

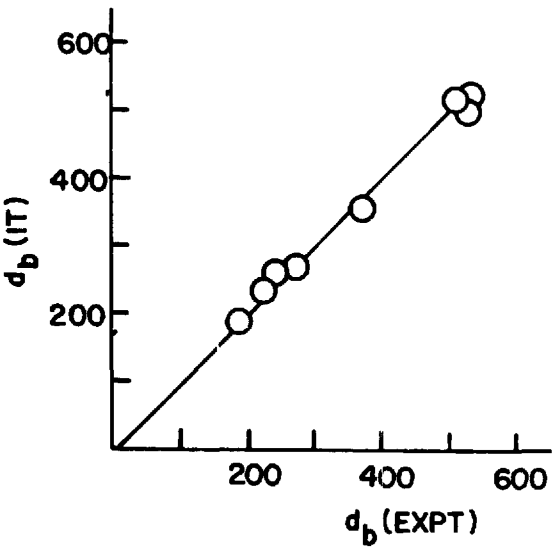

Fig. 2. d_b(It) versus d_b(Expt).

found by log-normal statistical treatment of actual sieve analysis data of the fine portion. The line has the equation:

$$d_b(\text{It}) = (1.02 \pm 0.03)\, d_b(\text{Expt}) - (7 \pm 9) \tag{7}$$

and hence does not differ significantly from the expected $d_b(\text{It}) = d_b(\text{Expt})$.

Full sieve analyses are usually cumbersome to perform and analyze but, as shown above, d_b can be obtained by iteration without the necessity for such an extended procedure. The data for the 14/20 mesh fraction in Fig. 3 are the mean diameters of the fine fraction, d_b, as a function of the amount of polyvinylpyrrolidone in the granulation. A general iteration procedure is used where consecutive estimates are made of the asymptote (d_e) in Fig. 3 (Carstensen, 1972; Carstensen and Su, 1972; Carstensen and Pothisiri, 1975). The value of d_e giving the least sum of squares ($(n-2)s_{yx}^2$) is the parameter value of choice. Values of s_{yx}^2 as a function of d_e estimates are shown in Table 2.

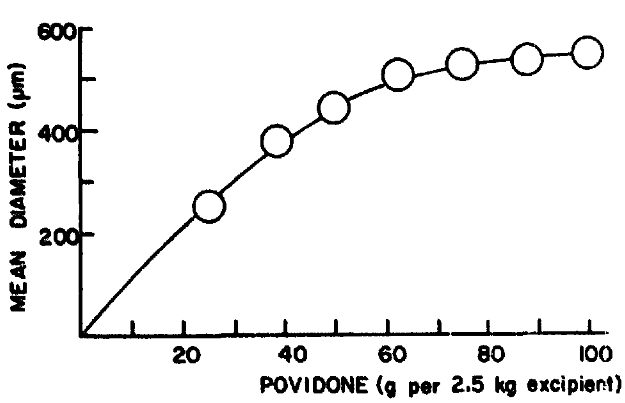

Fig. 3. d_b as a function of x.

TABLE 2

ITERATION VALUES FOR FITTING DATA FROM TABLE 1 TO ln (d_e–d_b) = –Fx + G

d_e (m)	560	565	570	575
s_{xy}	0.0598	0.0594	0.0590	0.1198
F	0.0410	0.0368	0.0343	0.0315
G	6.778	6.632	6.560	6.474

It is seen that the data follow the equation:

$$\ln(570 - d_b) = -0.0034\ x + 6.56 \quad (8)$$

Hence one can obtain an x_{90}, beyond which further addition of polyvinylpyrrolidone would serve no purpose by

$$\ln(0.9 \cdot 570) = -0.0034 \cdot x_{90} + 6.56$$

giving

$$x_{90} = 94$$

It is interesting to note as well, that when polyvinylpyrrolidone is added to the powder and then granulated with isopropanol, the correlations change. In essence the crushing strength of such a granule (about 330 g/mg for x = 40) although not very reproducible is higher than what would have been expected had the polyvinylpyrrolidone been added to the isopropanol and not to the powders. Adding the polyvinylpyrrolidone to the powder hence would appear (a) less reproducible, but (b) more efficient than the alternate method, presumably because it allows position of the polyvinylpyrrolidone at the position in the granule where the bonding occurs, and not elsewhere.

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