Size Distribution of Sugar Crystals

ANDREW VANHOOK[1]

Introduction

The size distribution of finished crystals is valuable for practical purposes, as well as for theoretical revelations concerning the mechanism of crystal growth. The former aspect, in the specific case of sucrose, is dealt with in Spencer-Meade's *Handbook* (18) ,[2] and Browne and Zerban (3) ; by Mr. Nees at the Denver meeting of this Society (11) , Mr. Fort in his *Reports of Studies on the Uniformity of Beet Sugars* (4) , Mr. Powers of Tate and Lylc, Ltd. (13), and by many others (12, 16, 19). The demands of the trade; and the influence of crystal size on behavior in the centrifuge, on packaging, handling, and caking, are considered in these several references.

The connection between size distribution and mechanism of growth has not yet been analyzed in the case of sucrose, to the writer's knowledge; and it is the purpose of this paper to consider this matter.

Results

Powers (13) has summarized the screen analyses of a variety of refinery products, and finds the arithmetic-probability plot to be linear between 10 and 90% (13a), or even better (13b), for most commercial products. The writer has plotted the screen data of several hundred examples from various sources (2, 4, 8, 13b, 19, 21a) , in many different ways (1, 5) ; and finds this same arithmetic-probability plot to be the most satisfactory manner of representation. It is linear, in most cases, between the 2 and approximately 90% values. Beyond these limits the deviations are generally of the nature indicated in Figure 3, and they arc seldom symmetrical on the high and low ends. These data are mostly for commercial products; which, Fort (4b) has pointed out, "are a mixture of strikes made from massecuites of widely variable purity — and may not yield consistent probability curves." The test in the case of individual strikes (13b, 19, 21a) is not only superior, but very significant in indicating the mechanism of the crystal generating and growth processes.

Discussion

Since the growth of sucrose crystals is proportional to the growing area (7, 10) , the Gaussian distribution, which is observed, immediately suggests a purely chance distribution (6, 15) of the originating centers of growth. This, of course, is exactly the situation in the case of any seeding procedure, and even in the case of boiling to grain as for many of Thieme's data (19) . It implies the induction of graining by inoculation, or via a heterogeneous process, and this is probably the case in usual sugar house work (21b) .

The observed distribution remains nearly normal when extraneous nucleation is avoided by careful vacuum evaporation without ebullition, as described by Schweizer (17) . This similar distribution seems reasonable
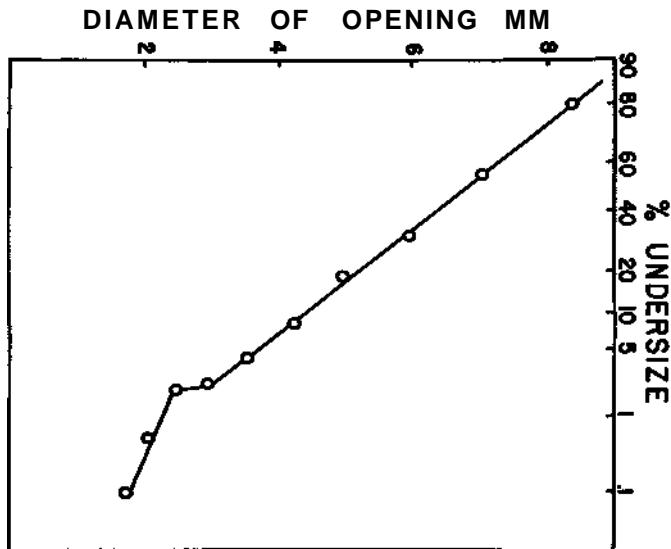
DIAMETER OF OPENING MM

Figure 1. Abnormal Type of Distribution Curve.

when it is recognized that the onset of nuclei formation is very sensitive to concentration changes—in fact, virtually critically so (21b) . This sudden establishment of a high concentration of nuclei of various sizes will depend upon the frequency of collision between particles, and it seems not unreasonable that this occurs according to kinetic theory, and, hence, is described by the normal distribution law (9, 15). This same behavior has been observed at concentrations below that required for normal, homogeneous nucleation, when prolific graining was induced suddenly by ultrasonic irradiation (20) . The size distribution was again normal, and, as in the above case, the uniformity was vastly better than that observed in commercial products: viz.

Coefficient of Variation (13) , or σ
Specified for standard granulated (13b) 20-25%

Homogeneously nucleated at an
Oversaturation of 1.6 ....14.8, 19.3%

Ultrasonic irradiation at 0 $\doteq$ 1.1
(Average of 4 trials) 11.7%

The above deductions and observations are completely in accord with the mathematical analysis of Roginski and Todes (14). These workers find that the normal type of size distribution results if crystallization proceeds from seeding without independent formation of nuclei, or when the rate of nucleous formation falls off rapidly with a decrease in supersaturation. This is not observed to be always the case with most substances (1), even though it represents the basic mechanism involved in nucleus formation and subsequent growth (22).

Several instances were encountered in the present survey in which distinct breaks in the normal probability curve were observed. Fig. 1 represents such a case. This abnormality is probably the result of the product being a blended mixture of otherwise normal components, or an interruption in the normal growth of a single strike. Loveland and Trivelli (9) have shown how these and related cases may be normalized by means of the *lognormal* distribution (6):

$$n = \frac{\Sigma n}{\ln \sigma \sqrt{2\pi}} e - (\ln x - \ln M)^2 / 2 \ln^2 \sigma$$

where n is the number of particles of size x, M the mean size, and σ the standard deviation. The conversion to weight fractions is readily carried out (1, 5, 11); although this is not necessary, since the function is independent of the size parameter. Physically, this modified frequency law is a skewed form of the normal Gauss law, and it emphasizes the seemingly independent portions of any composite curve as well as the dissymmetry at both ends.

In view of the success of the normal distribution function in describing most of the data on sucrose crystals, and in the lack of positive information about the unusual cases, a detailed analysis by Loveland and Trivelli's methods has not been attempted. The deviations from the normal curve on the fine and coarse ends are probably due to the removal of these extreme sizes by screening, as well as the occurrence of dust on the surface of larger particles. Fig. 2 illustrates this latter effect. Obviously these extreme fines will not be counted as such by the usual procedures; thus contributing to the low undersize values which are usually observed. If the size count is made on unscreened and undried product, the linearity on the small end is greatly extended. Likewise, the deviations on the coarse end are, presumably, due to agglomerates, and these are frequently apparent upon microscopic examination. If agglomerates are reduced by careful dispersion before measurement the linearity on the coarse end is improved, but the contrary effect increases on the other extreme. This is probably the result of attrition, for the same effect is noted when false grain is formed in ordinary boiling (19).

Figure 2. (See page 573). Electron Micrographs of Sugar Crystals (Confectioner's Grade A)
A. Original crystal, SiO_2 replica, 4200X.
B. Water Etched, SiO_2 replica, 4200X.
C. Water Etched, Formvar replica, Uranium shadowed, 7600X.
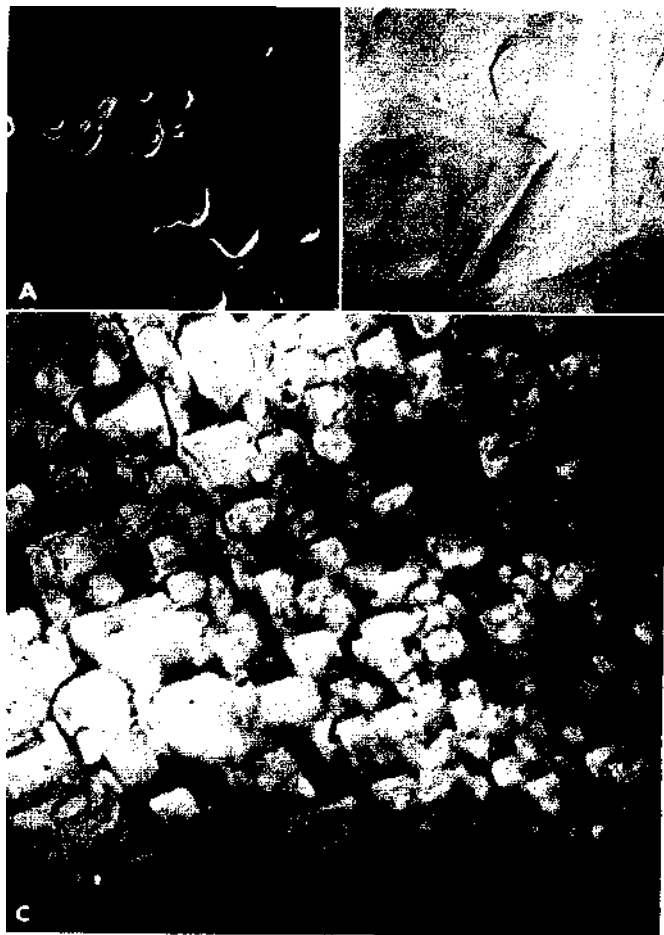(Courtesy Stamford Research Laboratories, American Cyanamid Co.)

Figure 2.

Both effects may be minimized by boiling a low purity strike (experimental) ; in which case agglomeration is greatly reduced. The linearity was observed to be vastly improved in this case, as evidenced in Fig. 3. In this plot a specific example of a similar size commercial product (13) is given for comparison.
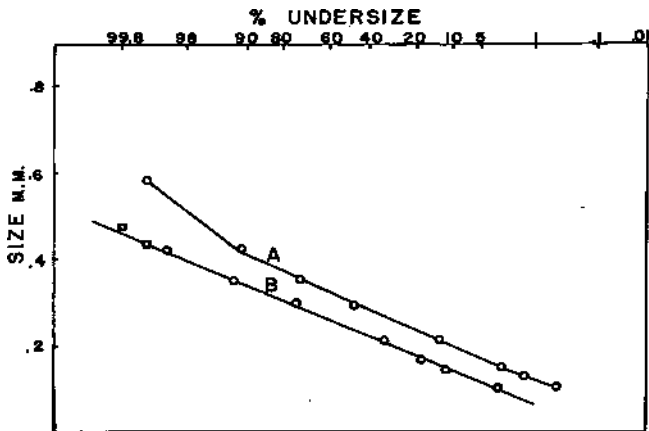

Figure 3. Frequency curves of high purity (A) and*low purity (B) strikes.
A—Caster grade, refined (13b)
B—Experimental strike, boiled to grain at 80° purity; Cuban stock, counted wet.
o—Screen sizes
•—Microscopic sizes

Summary

The size distribution of most sugar crystals follows the arithmetic-probability curve very well within wide limits. This suggests a heterogeneous mechanism of nucleation in the usual boiling procedure, and a critical dependence of nucleation on supersaturation when all foreign nuclei are excluded.

Occasional discontinuities may be accounted for by interruptions in the boiling or by the blending of finished products. Deviations at extreme sizes are accounted for by the previous removal of these sizes in commercial work and the presence of agglomerates and uncounted fines when these fractions are present.

Literature Cited

(1) AUSTIN, J. B.
        1939. Methods of Representing Distribution of Particle Size. Ind.
            Eng. Chem. 11 334.

(2) BROWN, J. M.
            Revere Sugar Refinery, Private Communication.

(3 BROWNE, C. A., and FERBAN, F. W.
        1941. *Sugar Analysis,* N. Y.

(4) FORT, C. A.
        (a) Chemical and Physical Studies on Beet Sugars, 1942, 1946, 1947
            and 1948 Campaigns—with S. Byall; U.S.D.' Agric. A.I.C. 29, 150,
            193 and 249.
        (b) Private Communication.

(5) HATCH, T., and CHOATE, S. P.
            Frequency Laws J. Frank. Inst. 207 369 (1929) ; 215 27 (1933)

(6) KAPTEYN, J. C, and VAN UVEN, M. J.
        1916. Skew Frequency Curves. Proc. Akad. Amsterdam 19 Sept.
            (1916) .

(7) KUCHARENKO, J. A.
        1928. Crystallization of Sucrose. Planter Sugar Mfg., May-June (1928) .

(8) LANG, L.
            National Sugar Refining Co., Private Communication.

(9) LOVELAND, R. P., and TRIVELLI, P. H.
        1947. Analysis of Particle Formation and Growth. J. Phys. and Coll.
            Chem. 51 1004.

(10) MCCABE, W. L.
        1929. Unit. Operation of Crystallization Ind. Eng. Chem. 21 30, 112.

(11) NEES, A. R.
        1946. (a) Sieve Tests and Fineness Modulus of Granulated Sugar.
            r^Proc. Am. S. Beet Tech. 4 565.
            (b) Private Communication.

(12) OWEN, W. L.
        1923. The Planter 70 68.

(13) POWERS, H. E. C.
        1948. (a) Determination of the Grist of Sugars. Int. Sug. J. 50 149.
            (b) Private Communication.

(14) ROGINSKI, S. Z., and TODES
            Kinetics of Crystal Formation. Compt. rend. acad. sci. (U.S.S.R.)
            27 677 (1940) Bull. Acad. Sci. (U.S.S.R.) 331 (1940); 106
            (1942) C. A. 35 1296, 5010.

(15) ROLLER, P. S.
      1937. Law of Size Distribution. J. Frank. Inst. 223 620.

(16) SANDERA, K.
            Fineness of Sugar. Z. Zuckerind, Cech. 62 217 (1936/7)

(17) SCHWEIZER, A.
      1933. A Contribution to Our Knowledge of Crystallization. Int. Sugar
      J. 35 385.

(18) SPENCER, G. L., and MEADE, G. F.
      1945. *Cane Sugar Handbook,* N. Y.

(19) THIEME, j. G.
      1928. Studies in Sugar Boiling. Facts About Sugar, N. Y.

(20) TURNER, C. F.
      1949. Ultrasonic Experiment; M.S. Thesis, College of the Holy Cross.

(21) VANHOOK, A.
            (a) Unpublished experiments.
      1949. (b) Nucleation and Growth in Sucrose Solutions. Farady Soc.
      Discussions No. 5.

(22) VOLMER, M.
      1938. *Kinetik der Pliasenbildung.* Steinkopf (Edward Bros.; Ann Arbor
      Mich.)

Acknowledgment