

Letters to the Editor

THIS section will accept reports of new work, provided these are terse and contain few figures, and especially few halftone cuts. The Editorial Board will not hold itself responsible for opinions expressed by the correspondents. Contributions to this section should not exceed 600 words in length and must reach the office of the Managing Editor not later than the 15th of the month preceding that of the issue in which the letter is to appear. No proof will be sent to the authors. The usual publication charge (\$3.00 per page) will not be made and no reprints will be furnished free.

On the Possibility of Estimating the Average Surface Area of Solid Particles

Hans M. CASSEL

General Ceramics and Sleatite Corporation, Keesbey, New Jersey

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IT would be easy to derive the average surface area of crystalline powders from the thermal effects caused by submersion into a suitable liquid if the heat of emersion per unit area were known. Since this is not the case it appears as a very ingenious idea to coat the crystalline particles with the adsorbed film of a liquid whose surface energy can be independently determined.

No objection shall here be raised against the principle of this method, but, unfortunately, the experimental procedure described by Harkins and Jura¹ implies a source of error which invalidates the reported results.

With the objective of surface conditioning single crystallites, the contiguous mass of the powder is exposed to the saturated vapor of a liquid and the entire system (presumably) allowed to attain thermal equilibrium. The powder treated in this way is then plunged into a body of the same liquid and the thermal effect observed.

In evaluating the measurements, it is assumed that the contact angle at the liquid-crystal-vapor boundary is zero. However, the point has been overlooked that under this very condition capillary condensation between the contracting crystals is inevitable. Consequently, in a thus treated powder, groups of particles may stick together, held by the capillary forces of the liquid. However, even the immediate cohesion of adjacent crystals may cause inseparable clusters to form.

Effects of this kind have been repeatedly investigated. Tomlinson² measured the adhesion between quartz filaments and concluded that the magnitude of the forces appears altogether too large for an explanation depending on the surface tension of a liquid film. Stone³ found that glass beads would not adhere unless the humidity is close to saturation, but once sticking together cannot be separated by passing dry air to remove the moisture. In the work of Bloomquist and Shutt⁴ it has been shown that microscopic glass spheres suspended in organic liquids are flocculated on increasing the amount of dissolved water. The coalescence is correlated to the magnitude of the

interfacial tension at the organic liquid-water film boundary. Bradley⁵ demonstrated a striking increase in the surface tension of concentrated suspensions caused by the mutual attraction of neighboring solid particles.

Taking all this into consideration, in the described procedure an indefinite reduction of the immersed film area has to be expected.

On the other hand, if capillary condensation is not accomplished the assumption of perfect wettability cannot be true. In that case, the heat of emersion per unit area would be smaller than anticipated and, again, the surface area would be underestimated.

Of course, such troubles would be avoided if it were possible to measure the thermal effects of particles individually coated and individually dropped into a liquid.

¹ William D. Harkins and George Jura, *J. Am. Chem. Soc.* **66**, 1362 (1944).

² G. A. Tomlinson, *Phil. Mag.* **6**, 695 (1928).

³ William Stone, *Phil. Mag.* **9**, 610 (1930).

⁴ C. R. Bloomquist and R. S. Shutt, *Ind. Eng. Chem.* **32**, 827 (1940).

⁵ S. R. Bradley, *J. Phys. Chem.* **43**, 663 (1939).

Ion-Migration Phenomena Observed with the Electron Microscope

HELMUT THIELSCH

University of Michigan, Ann Arbor, Michigan

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A DROPLET of water containing dissolved KCl (5 g per liter) was placed on a collodion film and then included into a vacuum system which was pumped down to 10^{-3} mm Hg within 30 seconds. Viewing the result in the electron microscope three rather curious types of structures are apparent, a regular cubic crystal structure (Fig. 1), a regular linear dendritic system (Fig. 1), and an irregular branch structure (Fig. 2). Obviously, the differences are due to the rate of nucleus formation and growth, depending, of course, upon the variation of local ion concentration within the droplet of water during the process of evaporation.

The first mentioned type of crystal (the cubes shown in Fig. 1) results from a relatively slow rate of growth; the second linear type will be produced by a somewhat faster rate (its closeness to the more stable cubic crystals signi-

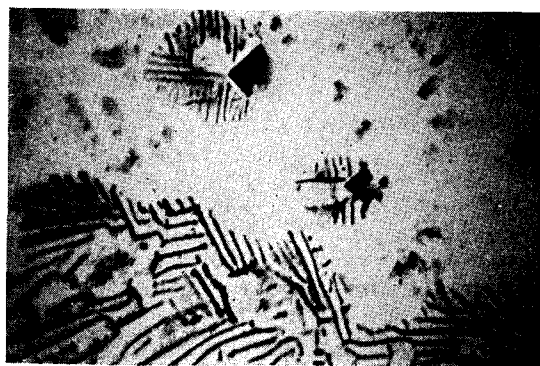


FIG. 1.



FIG. 2.

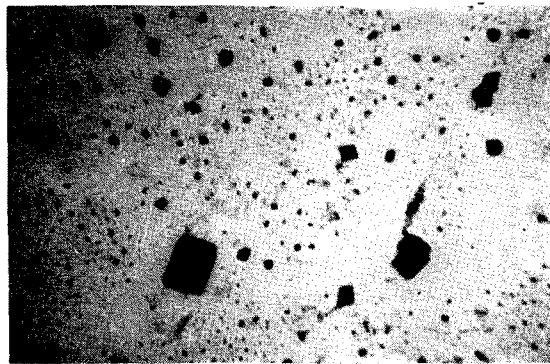


FIG. 5.

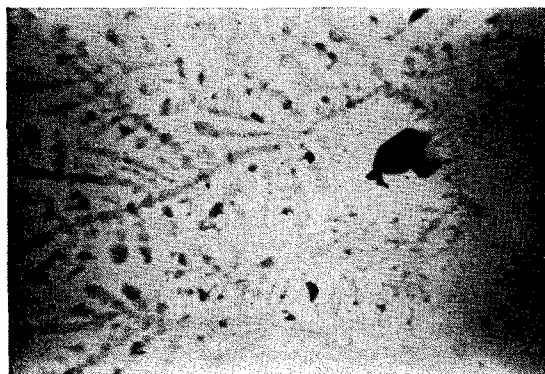


FIG. 3.

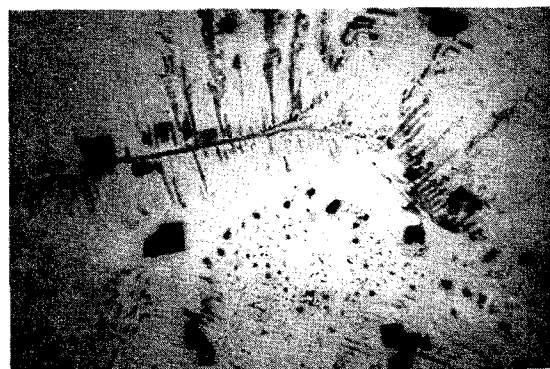


FIG. 6.

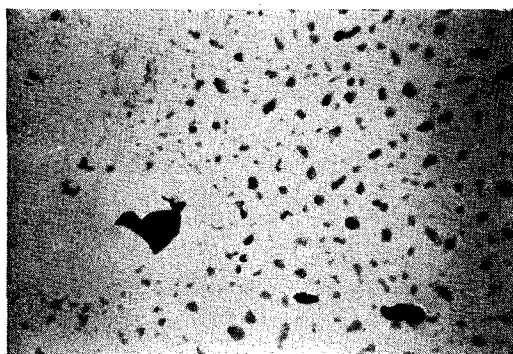


FIG. 4.



FIG. 7

fies that), and the irregular dendritic branch structure requires a still faster rate.

The two dendritic structures are unstable in atmospheric conditions, since upon standing for 6 hours in the atmosphere (Figs. 3 and 4), or merely breathing upon the sample (Figs. 5 and 6) will cause migration. In the last two figures outlines of the previous structure are still visible.

Whether or not the streaks or schlieren which appear in regularly grown crystals (Fig. 7) are identical with the linear dendrites observed or are due to electric surface charges,* further investigations will have to bring out.

A detailed discussion of this will follow in the near future.

* H. Seemann, "Die wandernden Schlieren in elektronenoptischen Bildern von Einkristallen, insbesondere Molybdanoxyd," *Naturwiss.* 31, 415-416 (1943).