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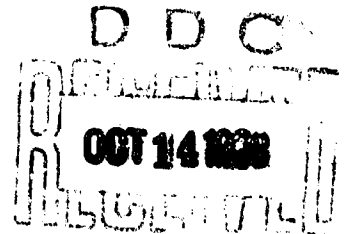
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DEPARTMENT OF THE ARMY
Fort Detrick
Frederick, Maryland

DETERMINATION OF THE SPECIFIC SURFACE OF SUBLIMATED

METALDEHYDE

K.Bisa and E.Kruecke

1. Preparation

The preparation,obtained by sublimation,was flaky, snow-like and typical for this type of sublimation(1). The flakes were placed on a glass slide,carefully covered with a cover slip in order not to damage the crystalline needles and sealed with Eukitt(2).

The first photomicrographs were taken with a Zeiss microscope and attached camera and they showed the crystals were heavily matted (Figure 1). With greater magnification, especially of crystals lying at the edge of the preparation, crystalline needles of uniform thickness,but highly variable length could be seen(Figure 2).

Fig.1 see text

Fig.2 see text

2. Theory

In view of the heterogeneity of the crystals, it seemed difficult to determine directly the specific surface area, i.e. the surface area per gram of substance. Consequently, the following simplefied model was postulated: the crystalline needles are cylindrical in shape and several times longer than wide, having the diameter d_s. In this case, the formula for the specific surface area becomes

$$S_W = \frac{4}{Q \cdot d_s} \qquad (Q= \text{density}) \quad (3,4) \quad /1/.$$

When the edges were ignored, at least a portion of the diminished surface area, caused by the matting of the crystals, could be considered. The density of metaldehyde is said to be 1.27, according to Hassel and Mark(5), but 1.31 according to the crystal structure determined by Pauling and Carpenter(6). Our formula permits the determination of the specific surface by a single measurement of the thickness d_s of the crystalline needle.

3. Microscopic Determination of Crystal Thickness

All photomicrographs were taken with an Orthomat microscope-camera combination(manufactured by E.Leitz, Wetzlar),equipped with ? P. Apo Oil 90/1.15 objective, 90 X magnification,oil immersion,in a phase-contrast micro-scope with an arc lamp and a green filter. Total magnificat-ion was determined by photographing a stage micrometer, divided into 0.01 mm, with the same objective to 378.

Twenty-nine photographs were evaluated and the thickness of 335 crystalline needles was measured. A measuring microscope,Leitz TBS 50 (35 X magnification) was used,because of the small size of the diameter. The accuracy of three measurements, done each time, was about 3% and, in some cases, 5%. Since the thickness of the crystal surpassed the lateral melting tendency by about 0.30 micron,the photographs show typical,bright halos of weak phase contrast. Considering the unavoidable falsification of the picture(a weakness of the objective),the micrometer was always centered in the middle of the clear halo(7,8). On account of the axial melting ability of about 0.54 micron,only a portion of the crystal appeared sufficiently sharp under the microscope and suitable for measuring the thickness(compare Figures 3 and 4, taken in slightly different focal planes).

Fig.3   see text

Fig.4   see text

Photographs taken in the center of the flaky preparation which was obviously strongly matted(Figure 5) showed that the thickness of needles there was similar to that of needles near the edge of the preparation(Figures 3 and 4). A tendency to form twin-needles and large aggregates can be seen in Figure 6. In such cases, only the thickness of a "single" was measured. Some needles had a length which extended over several microscopic fields.

Fig.5   see text

Fig.6   see text

The frequency histogram, shown in Figure 7, shows a maximum thickness of about 8×10^{-5} cm, i.e. 0.8 micron, and skewness towards increasing thickness. The locations of the minima and a second maximum at about 1.6 micron are noteworthy. The minima are discussed later on. The second maximum may have been caused by the inadvertent measurements of twin crystals which cannot be easily spotted, especially near the edges of the photomicrograph.
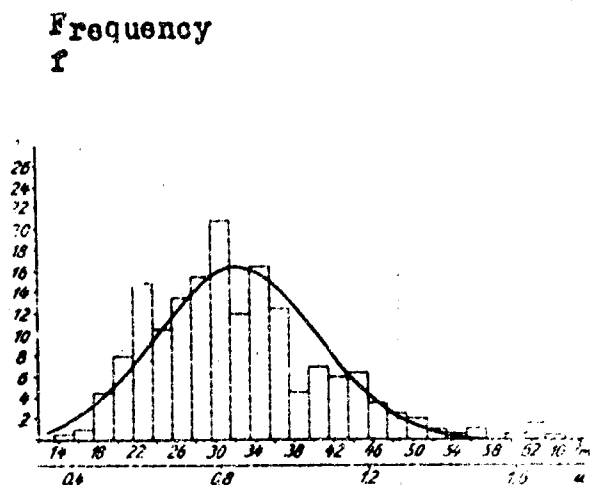
Frequency
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Fig.7. Frequency distribution
of thickness d_S of crystals
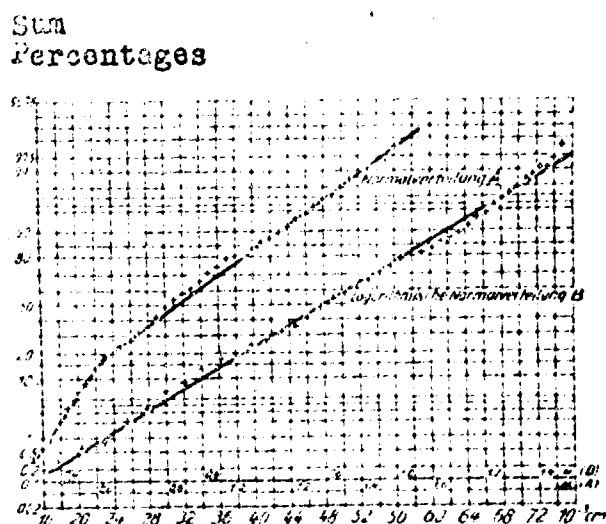(normal curve is shown for
comparison)

Fig.8.Plotting the sum per-
centages on probability paper
A = normal distribution
B = logarithmic normal distribut-
ion

The calculation of the average gave $f.x/n = 8.51 \times 10^{-5}$cm,
with a standard deviation of $\sqrt{f.x^2/n} = 2.36$, or 2.14×10^{-5} cm,
depending on whether or not the second maximum at 1.6×10^{-4} cm
was included. When the sum of percentages curve was plotted on
probability paper,using either equidistant divisions(normal
distribution) or logarithmic divisions(logarithmic normal
distribution) neither approach showed complete agreement(Fig.8).
However,the observed distribution was better approximated by
the logarithmic normal distribution curve(average $d_S = 8.0 \times$
10^{-5} cm, standard deviation = 2.0×10^{-5} cm). By using the
density value of 1.27 of Hessel and Mark(5) for metaldehyde
and by applying formula /1/,the specific surface was experi-
mentally determined to be

$$S_w = \frac{4}{1.27 \times 8.51 \times 10^{-5}} = 3.7 \times 10^4 \text{ cm}^2/g.$$

4. Discussion

Although the length of the crystals showed considerable
variability,the thickness was relatively uniform. Obviously,
the growth in length was stronger than the growth in width.
As soon as the needles reached a certain thickness,growth in
that direction slows down,it seems,but continues in length.

Probably, the difrerential tendencies of growth rates with
respect to difrerent directions can be explained by the
tetragonal crystal structure of metaldehyde. The space-
centered elementary body with eight acetaldehyde molecules
(space group C_4^5) has the dimensions $a_o = b_o = 10.40$ Å and
$c_o = 4.11$ Å (6,9)[4]

In this connection, it is of interest to note the
recently discovered tendency of metaldehyde to form the
nucleus in ice crystal formation(10). This tendency is shown
by metaldehyde and nonisometric substances,e.g. silver iodide
(at ordinary temperature),cobalt iodide and cadmium iodide.

Statistical results were of crucial importance because
of the high variability of the crystalline needles in the
preparation. As already mentioned earlier,the same thickness
existed in the center and on the edges of the preparation of
the needles.

If the irregularities of the decreasing portion of
the frequency histogram are real,they may have been caused
by not considering the length of the crystals. Beirne and
Hutcheon(11) who examined the shape of coke particles also
found similar deviations in their histogram. Coke is also a
flaky particle(width and thickness about equal,but both much
smaller than the length). Considering the "flakiness"(12)
requires the additional consideration of crystal length.
Formula /1/ describes an idealized model of a cylindrical
particle with a length much longer than the width and,actually,
cannot be applied. The dimensions of the shape ought to be
determined by independent measurements. Occasionally,variation
in thickness may also occur among particles of average size.

The measured thickness of the crystals showed the
relatively large deviation of about 25%. It must be assumed
a modification of the method of sublimation(variation in
the speed of the process,variation in the difrerence of the
temperature of steam and condensing surface) may influence
the tendency of growth in two directions on the part of the
crystalline needles.

5. Summary

The specific surface of sublimated metaldehyde was determined microscopically on the basis of a simplefied mathematical model and known density and was derived from the thickness of the crystals. The deviation of the distribution of crystal thickness from the normal curve was discussed. It was assumed that the tendency of metaldehyde to grow differentially in two directions at different rates was based on the nonisomeric crystal structure and was also influenced by the conditions of the sublimation method.

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