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Isothermal and NonIsothermal Transformations of TactoidForming Particles of Tungstic Acid

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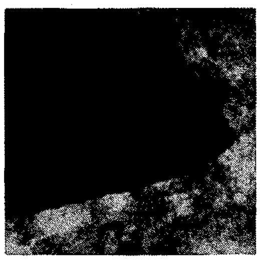

FIG. 2. Electron micrograph of the edge of a tip of a tungstic acid particle, ×12,000, showing toothed edge.

particles are frequently not smooth, but toothed (Fig. 2). In the example given, each of the remarkably uniform "steps" has a length of slightly less than 400A in the direction of the major axis. On the assumption of a tactoid-like structure, the elliptical shape could be explained as the result of an anisotropy of interfacial energy or as the result of a competition between the interfacial energy and the exceedingly weak (long-range distances!) "lattice" energy of a tactoid. If the particles represent crystals of anomalous shape, then they are related to the "somatoids" described by Kohlschuetter.[4] Generally, however, the elliptical species of somatoids does not have a shape as regular and uniform as observed in the above systems.

After a sufficient aging of the respective suspensions, particles of "type *D*" are found exclusively (Fig. 1D), i.e., exceedingly thin perfectly regular-shaped rectangular crystals. The morphological differences between the two types of particles is apparent not only in the dried-out samples studied electron-optically, but also in the original samples investigated with the polarizing light microscope. A comparison of the sharp electron diffraction diagrams obtained from particles of type *D* with the less distinct ones exhibited by particles of type *A* indicates definite differences in intrinsic structure, in addition to the morphological differences.

At intermediate ages of the suspensions, platelets of intermediate shape are observed. For purposes of statistical evaluation, we divide them into two general types: type *B* (Fig. 1B) representing particles with straight plane-parallel edges at the midsection, whereas the end sections are still elliptically curved, and type *C* (Fig. 1C) representing octagonal particles with straight edges throughout. Occasionally, irregularly shaped variants of these four general types and also twins and triplets are observed, but they are statistically unimportant. (The absolute sizes of the particles in the four photographs of Fig. 1 cannot be compared because they were obtained from suspensions of different history (see a subsequent communication).)

The existence of the intermediary types *B* and *C*, the fact that the size distribution curves compiled as a function of the age of the suspensions do not show characteristic changes or discontinuities, and the absence of definite double distributions seem to make it certain, in addition to other findings, that the particles of type *D* do not develop from dissolving particles of type *A*, but rather by their slow transformation.

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[1] H. Zocher and K. Jacobsohn, Koll. Beih. **28**, 167 (1929); H. Zocher and W. Heller, Zeits. f. anorg. allgem. Chemie **186**, 75 (1930).
[2] W. Heller, Comptes Rendus **201**, 831 (1935); P. Bergmann, P. Loew-Beer, and H. Zocher, Zeits. f. physik **A181**, 301 (1938).
[3] See also W. Feitknecht, Vierteljahrsschrift Natur. Ges. Zuerich **161**, XC (1945).
[4] E.g., V. Kohlschuetter, C. Egg, and M. Bobtelsky, Helv. Chim. Acta **8**, 457 (1925).

Isothermal and Non-Isothermal Transformations of Tactoid-Forming Particles of Tungstic Acid

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FIGURE 1 shows on two representative samples that the isothermal habitus change (25°C) $A \rightarrow B \rightarrow C \rightarrow D$ of the particles which develop from a solution of tungstic acid[1] is accompanied by a continuous increase in the major axis (length) of the particles. The rate of change of both habitus and size are found to be highest shortly after the organization of elliptical particles (nuclei), 0.2–0.3-micron long, from electron-optically unresolved amicronic material. No nuclei have been observed in solutions less than two hours old. The results support the concept[1] that the particles of type *D* develop directly from particles of type *A* by a morphological change of the latter.

The hydrogen ion concentration decreases very strongly with increasing age of the suspensions, i.e., with the progressing development of the particles. One example is given in Table I. This is due primarily to the fact that the particles develop from tungstic acid in solution, but part of the effect apparently must be attributed also to the transformation of the particles themselves. Particularly interesting is the fact that the rate of change in habitus is faster (Table II) and the final size is smaller (Fig. 1) the lower the initial hydrogen ion concentration. (The latter is varied by varying the concentration of HCl which is present beside tungstic acid.)

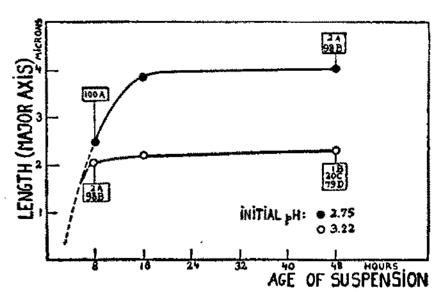


FIG. 1. Change in length (major axis) of the platelets of tungstic acid with the age of the suspensions. (Inscription in squares: percentage frequency of the four types.)

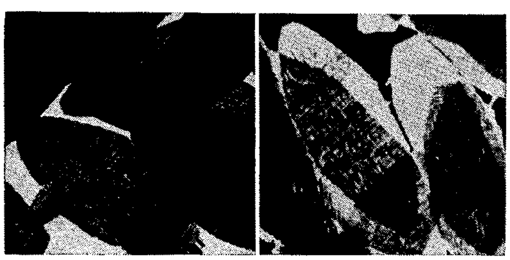
TABLE I. Change of pH with the age of suspensions of tungstic acid.

Age (days):	0	3	8	16	35	240
pH:	3.22	3.77	4.49	4.71	4.96	5.03

A qualitative change in the electron diffraction pattern accompanies the isothermal morphological transformation of the particles. This suggests that the change in habitus is accompanied by and most likely is a result of an internal transformation. Such isothermal internal transformations of colloidal particles had been known before, the most extensive one being probably the transformation FeOCl→ β-FeOOH→α-FeOOH, proved by x-ray diffraction and by magneto-optical measurements.[2]

This hypothesis is supported by the fact that the particles of type D evaporate uniformly under concentrated electron bombardment like typical anhydrous crystals. This suggests that they consist of single crystals of WO_3. Particles of type A, which definitely consist of tungstic acid, change, under electron bombardment, into a fibrillar structure of nematic symmetry which shows surprising sudden changes in the direction of the symmetry axis with respect to the major axis. This is illustrated in Fig. 2A and Fig. 2B on two different samples. The average distance between the centers of the "rods" is similar to the width of the steps observed in the contours of unbombarded particles.[1] This appearance of a fibrillar structure may favor the assumption of a tactoid-like structure for the unbombarded particles.[1] However, the possible sudden changes in the symmetry axis, under maintenance of a simple elliptical shape, in conjunction with the fact that the unbombarded particles show uniform neutral lines in the polarizing microscope,[1] suggest that at least the mosaic pattern, if not the fibrillar structure as such, is a quality of the particles produced by the electron bombardment.

Thermal heating and light microscopic observations of the changes produced leads to related results supporting the contention[3] that the effect of electron bombardment observed is a heating effect. Rapid heating to 650°C leads to a disintegration of the particles of type A into rectangular flat rods whose length is often of the same order of magnitude as the major axis of the original particles. Slow heating produces much shorter rods, apparently because of the lateral breakup of primary long rods. In either instance, the positive double refraction of the individual rods is uniform and much stronger than in the original particles. (Melting of the elliptical particles prior to or instead of their breakup also leads to a strong increase in double refraction with irregularly changing neutral lines.) Although a fibrillar structure of the elliptical particles could not be observed prior to their break up, according to Fig. 2, it actually is below the resolving power of a light microscope; it is safe to assume that the two phenomena, revelation or production of a fibrillar structure by electron bombardment and a break up under heating in the polarizing microscope, are conjugate. They apparently accompany the non-isothermal transformation of tungstic acid to tungstic oxide, under loss of water.



A B

FIG. 2. Electron micrographs to show effect of electron bombardment upon tungstic acid, ×10,000, (A) after bombardment, bright field, and (B) after bombardment, dark field.

TABLE II. Shape distribution, in percent, as a function of the age of suspensions of tungstic acid (number of particles considered: 2357).

Initial pH \ Hours	8	16	48
2.75	100A	2A 96B 2C	80B 10C 10D
3.00	23A 77B	1B 99C	8B 76C 16D
3.22	2A 98B	4B 82C 14D	1B 20C 79D

[1] J. H. L. Watson, W. Heller, and W. Wojtowicz, J. Chem. Phys. preceding letter.
[2] W. Heller, O. Kratky, and H. Nowotny, Comptes Rendus 202, 1171 (1936).
[3] J. H. L. Watson, J. App. Phys. 19, 713 (1948).

Direct Electron Microscopic Thickness Determinations of Ultramicroscopically Thin Crystals

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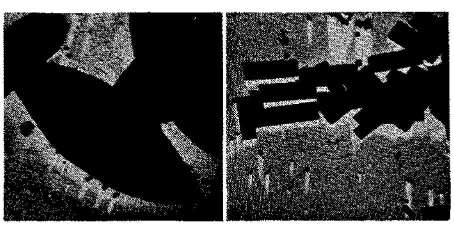
THE shadowcasting technique makes it possible to obtain the thickness of microscopic or ultramicroscopic particles indirectly. This technique was applied to the ultramicroscopically thin platelets which form from a solution of tungstic acid.[1] Examples for particles of type A and type D[1] are given in Figs. 1A and 1B, respectively. Chromium shadowcasting was carried out under an acute angle of less than 15°. Carbon particles, visible in the photographs, had been mixed with the preparation for calibrating purposes. The dimensions of the major axis,



(A) (B)

FIG. 1. Electron micrographs of chromium shadowcast tungstic acid ×2667.