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Experimental Study of the Coercive Force of Fine Particles

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The experiments described test the theory of fine-particle magnets. Particles of Fe, Co, and Ni, of size 100–2000A, were prepared by electrodeposition into a mercury cathode. Their sizes and shapes were determined with an electron microscope. Experiments on coercive force *vs* particle size show, in general agreement with theory, that the maximum coercive force of Fe particles occurs at about 150A and is about 1000 oersteds, for very small packing factors. The coercive force decreases rapidly for smaller particles, slowly for larger particles. The rapid decrease for particles smaller than 150A is attributed to thermal fluctuations; this is borne out by measurements at low temperatures.

Addition of 25 percent by weight of 20-oersted Fe particles to 1250-oersted Fe particles decreases the coercive force to 500 oersteds: thus any experiment designed to check the predicted 10 000 oersteds for particles of 10-to-1 shape anisotropy requires an extremely high percentage of such particles. For both Fe and Co, the temperature variation of coercive force closely follows that of crystalline anisotropy and not that predicted for particles with shape anisotropy. Electron micrographs show that many of these particles are bean-shaped, with axis ratio 1.5. The extent of the present work is not sufficient for evaluation of the contribution of shape anisotropy to the coercive force of Fe.

DURING the past fifty years there have been several independent investigations[1–5] of the ferromagnetic properties of small particles of iron, nickel, cobalt, and manganese bismuth. These investigations have shown extremely high coercive forces, of the order of 1000 oersteds for iron; and theoretical investigations have predicted coercive forces of ten times these experimental values.

What seems to be lacking is (1) the experimental relationship between the coercive force and particle size for iron, cobalt, and nickel, and (2) the exact shape of the particles that have a coercive force more than twice the value predicted by theory.

In order to obtain these relationships, fine particles of iron, cobalt, and nickel were prepared by the electrodeposition of these materials in a mercury cathode by use of standard electrolytes. The coercive force of the freshly deposited iron and cobalt could be made as low as 20 oersteds and subsequently increased to a maximum of 1000 oersteds by heating at a convenient temperature for a period of time. Further heat treatment would decrease the coercive force to as low as 40 oersteds. Figure 1 shows the relationship between the coercive force at liquid nitrogen temperature and time of heat treatment at 200°C.

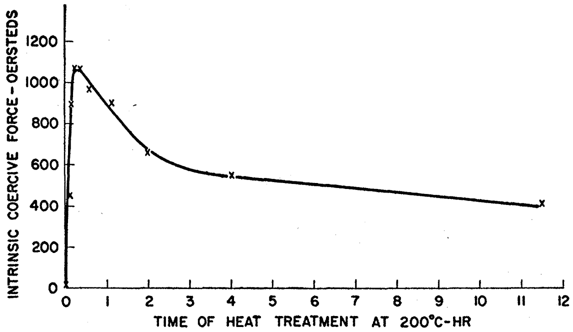

FIG. 1. Effect of heat treatment on the intrinsic coercive force of iron electrodeposited in mercury.

In order to measure the coercive force of the iron particles in the mercury it was necessary to prevent their movement or rotation by solidifying the matrix. This could be done by adding an alloying element such as silver to the mercury to obtain a solid matrix, or simply by freezing the mercury. Since experiment showed that the same coercive force was obtained by both methods, the latter method was used because it proved to be more expedient. The mercury was frozen by placing it in liquid nitrogen, and the coercive force was measured at this temperature.

In all cases, the coercive force listed is the intrinsic coercive force, measured by placing a magnetized sample in a coil immersed in a magnetic field which is directed opposite to that of the sample. The coil is connected to a galvanometer, which is caused to deflect by moving the sample in and out of the coil, yet keeping the sample in the reverse field. The reverse field is increased until no deflection is obtained, and therefore the intrinsic induction in the sample has been reduced to zero. The reverse field is then measured to obtain the intrinsic coercive force.

The above process gave excellent control of the coercive force, and as it happened also the particle size, so that a material was available for coercive-force and particle-size measurements. The measurements of the particle size, while the particles were still wetted by the mercury, proved to be both extremely difficult and unreliable. To remove the mercury from the particle by evaporation always resulted in a large particle size, as discussed in connection with Fig. 1. The best method of removing the particles and having the desired size was

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[1] H. Nagaoka, Wiedemann Ann. Physik **59**, 66 (1896).
[2] K. Honda, Japan Nickel Rev. **5**, 517 (1937).
[3] R. S. Dean and C. W. Davis, U. S. Patent 2,239,144.
[4] F. Pawlek, Metall. **1950**, 58.
[5] B. Kopelman, Elec. Eng. **71**, 447 (1952).

to dewet the particles by diffusing oxygen through the mercury, to form an oxide shell around the particles, and collect them after they floated out of the mercury. The use of a "Mercury Oxifier" has proved very efficient in this respect. Since this removal takes place at essentially room temperature, the particles do not grow in size except for the volume increase due to the oxygen taken on by the surface to form FeO. One might expect that the particles would be completely oxidized, but this does not happen except for the very small sizes below 50 A. If the powder is pressed in a die it has an extremely metallic appearence, and both electron diffraction and x-ray diffraction data have shown that the material is not completely oxidized.

A comparison of the coercive force of the particles in the mercury and after removal by the introduction of an oxide shell on the particles is shown in Table I for iron. The room temperature value of the coercive force is also shown along with the percent change due to the temperature difference. One might expect a shift in the maximum coercive force of the oxide-coated material toward the apparent larger particle sizes. Any such shift might easily be offset by having a particle-size distribution in the mercury, in which case the larger particle would be the first to come out owing to the greater buoyancy force. Because of these opposing factors, a correction has not been made in the particle size to account for the oxide shell on the particle.

TABLE I. Intrinsic coercive force of iron.

Hci in mercury −196°C	Hci out of mercury −196°C	Hci out of mercury 20°C	Percent change in Hci 20°C to −196°C
450	590	35	1600
900	1025	670	53
1075	1100	880	25
1050	1050	850	23
975	1000	870	22
900	850	750	14
350	350	300	17

The percentage difference in the coercive force shown in Table I is in good agreement with what one would expect from crystalline anisotropy. The one exception is the case of the particle of 35 oersteds at room temperature (75 A diameter), in which case one must turn to some explanation such as that proposed by Néel. The critical particle diameter for thermal instability decreases as the temperature is decreased, and hence a judiciously chosen particle would have a tremendous increase in coercive force as the temperature is lowered. This condition was found to exist also in the iron particles in a mercury matrix, where the coercive force of particles smaller than the optimum size increased from 400 oersteds at liquid nitrogen temperature to 550 oersteds at liquid hydrogen temperature and 700 oersteds at liquid helium temperature.

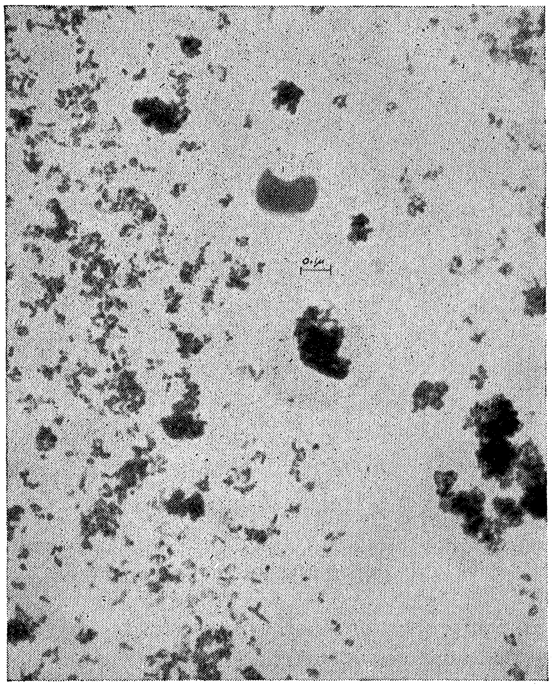

FIG. 2. Electron micrograph of iron particles in silicon monoxide.

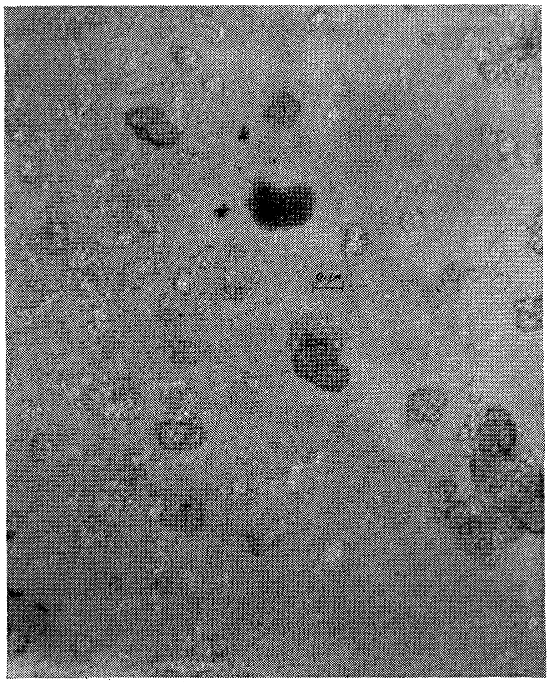

FIG. 3. Electron micrograph of same area as Fig. 2 after dissolving the iron particles to form a cavity. Some particles that have not been dissolved can be used as size reference.

The oxide-coated particles were prepared for measurement in an electron microscope, the first major problem being to show the effect of these small permanent magnets on the electron beam. It seemed very likely that the magnetic field of the particle would deflect the electron beam and cause the image not to be

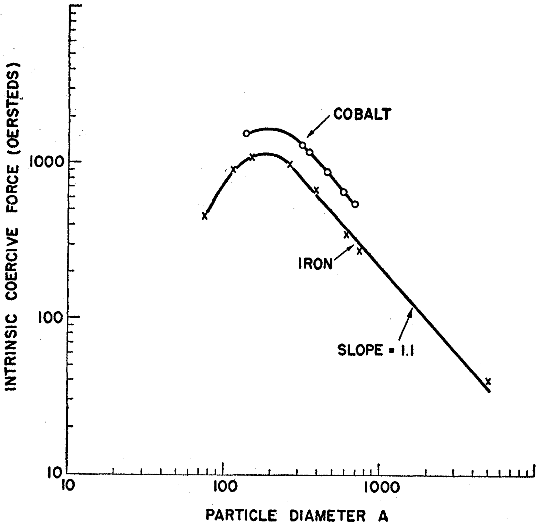

FIG. 4. Intrinsic coercive force at liquid nitrogen temperature of iron and cobalt particles as a function of particle size.

in direct proportion to the particle size and shape. Electron micrographs taken of the particle and of the cavity left after etching the particle from a silicon monoxide matrix show that the image does faithfully reproduce the size and shape of the particle. This is shown in Fig. 2 and Fig. 3.

The results of the measurement of particle size were plotted against coercive force and are shown in Fig. 4. It is apparent here that in the region from 5000A particles to 200A, where thermal fluctuations take over, the product of the coercive force and particle diameter is a constant and the curve is that of an equilateral hyperbola. This is in agreement with the relationship that Guillaud found for manganese bismuth particles. The present theoretical relationships of the simple theory of coercive force do not show this dependence of coercive force on particle size.[6]

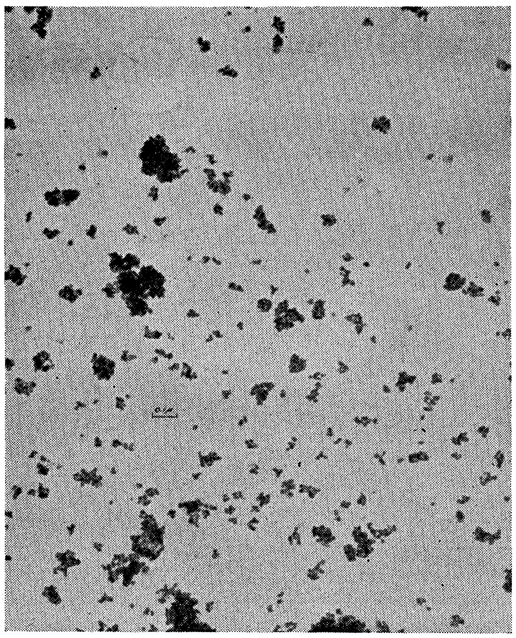

FIG. 5. Electron micrograph of 115A iron particles.

The straight-line portions of the curves shown in Fig. 4 will probably extend to particles smaller than 200A and then become horizontal if the measurement is made at a sufficiently low temperature to eliminate the drop due to thermal fluctuations in the particles.

The curve for particle size *vs* coercive force for cobalt shown in Fig. 4 gives a value of the critical particle size for single domain behavior which is of the same order of magnitude as for iron, and not ten times the size of iron as has been predicted by theoretical calculations.[6] There is also disagreement, as has been known for some time, between the experimental values of the coercive force for cobalt and the value obtained from consideration of the crystalline anisotropy energy. Theoretical calculations[6] predict a value of 6000 oersteds for cobalt on the basis of its crystalline anisotropy, while the experimental value is of the order of 1000 oersteds.

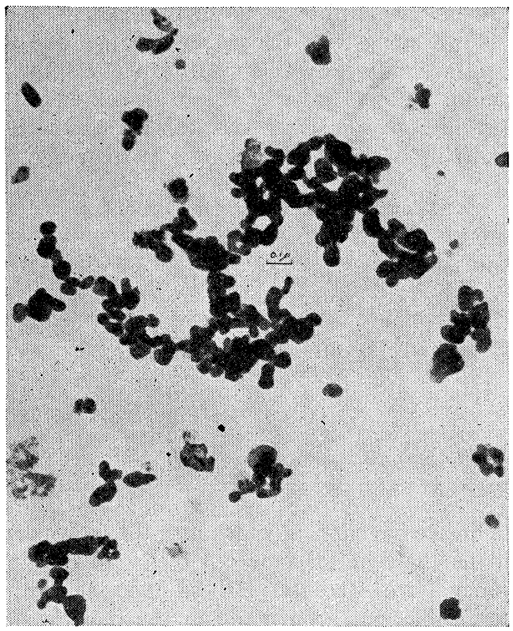

FIG. 6. Electron micrograph of 560A iron particles.

The shapes of the particles are shown in Figs. 5, 6, and 7. An examination of these electron micrographs shows that many of the particles have a shape anisotropy of 11/2 to 1. Of course, this is only a two-dimensional view of the particles, but a lack of any plate-like particles leads to the belief that these particles are nearly prolate ellipsoids of an axial ratio of 11/2 to 1. Since

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[6] C. Kittel, Revs. Modern Phys. **21**, 541 (1949).

theory [6–8] predicts a value of nearly 3000 oersteds for this ratio of major to minor axis of the particles, there again seems to be disagreement with the theory. Since there is certainly a size and shape distribution of particles shown in the electron micrographs, an experiment was conducted to determine the effect of this on the measured coercive force. The results are shown by Fig. 8.

To determine this relationship, iron was electrodeposited into mercury so as to have a coercive force of 12 oersteds. Since the suspension of iron in mercury is very homogeneous for this particle size, volumetric ratios were taken as a measure of the amount of iron in the mercury. Eight different samples were taken. Four of these samples were heat treated to have a coercive force of approximately 1000 oersteds at liquid-nitrogen temperature. These samples were then mixed with the untreated samples to form the required percentage of low- and high-coercive-force material (0, 25, 50, 75, and 100 percent of the former). The results of this procedure are given by curve 1 of Fig. 8. Essentially the same procedure was used to mix the untreated iron with cobalt heat-treated to near the maximum coercive force, and the result is shown in Fig. 8, curve 2. In both cases there is a rapid decrease in the coercive force with a small percent admixture of the low-coercive-force material. On the other hand, if iron of near-maximum coercive force is mixed with iron particles heat treated beyond the maximum to 150 oersteds and approximately 1000A particle size, the effect on the coercive force is greatly reduced. This result is shown in Fig. 8, curve 3. The decrease in coercive force is linear with the weight percent of low-coercive-force material, instead of having the shape of an equilateral hyperbola as in the case of very small particles of low-coercive-force material.

To explain the 1000 oersteds coercive force obtained for iron on the basis that there is a mixture of low-coercive-force particles (that is, some that are round and of 500 oersteds coercive force) with 3000-oersted particles of $1\frac{1}{2}$ to 1 shape anisotropy would actually require data similar to those shown in Fig. 8 for particles of similar size but of about 10 to 1 ratio of coercive force. However, if it is assumed that this relationship would be the same as for curve 1 of Fig. 8, which is more favorable to the theory, then the electron micrographs must show approximately 25 percent by weight of the particles to be round, smaller than 75A, or larger than 500A. The electron micrographs cannot be evaluated very well to show that there is not a 25 percent by weight of round particles. Also it is extremely difficult to evaluate the percent by weight of particles less than 75A because this size approaches the resolution of the electron microscope.

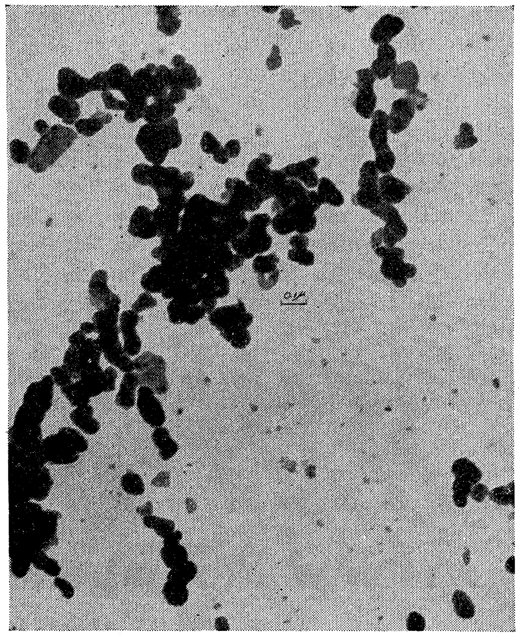

FIG. 7. Electron micrograph of 620A iron particles.

It is hoped that stereographic electron micrographs can be taken that will allow an evaluation of the true coercive force of the particles having shape anisotropy.

There is still another evaluation to be made, and this is the effect of clustering of the particles. In spite of the measurements being made at 0.004 packing factor (the weight of iron per cubic centimeter divided by the density of iron), the particles have not been separated any better than is shown in these electron micrographs, where it is obvious that there is considerable clustering of the particles into groups as great as 100 particles.

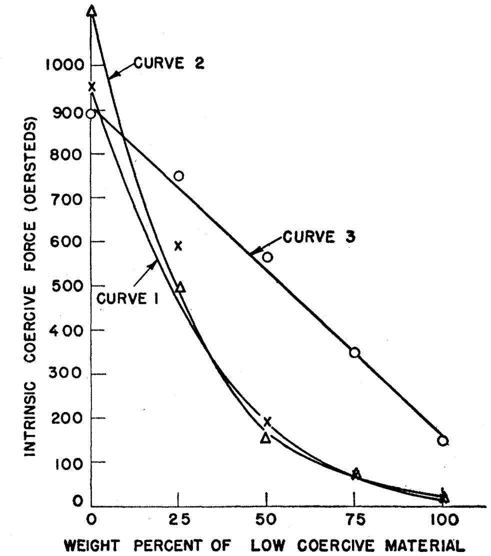

FIG. 8. Effect of mixing low coercive force particles with high coercive force particles.

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[7] E. C. Stoner and E. P. Wohlfarth, Trans. Roy. Soc. (London) **A240**, 599 (1948).

[8] E. Kondorskii, Doklady Akad. Nauk SSSR (N.S.) **70**, 215 (1950).

One can probably assume a packing factor of the order of 50 percent for these clusters, whereupon Weil[9] has shown that the coercive force will be cut in half. In addition, this clustering makes it extremely difficult to line up the particles. If we assume that Néel's[10] calculation for randomly oriented cubic crystallites applies to both hexagonal cobalt and iron with shape anisotropy, then the theoretical value for iron particles of 1½ to 1 shape anisotropy is reduced from 3000 oersteds for widely separated particles to approximately 500, and that for cobalt particles from 6000 oersteds to 1000 oersteds.

It is apparent that in spite of having particles of 1½ to 1 shape anisotropy, steps must still be taken (1) to better evaluate the effect of shape and size distribution, (2) to evaluate the effect of clustering on lining up of the particles, and (3) to evaluate the "apparent" packing factor due to clustering.

It is hoped that further work along these lines will lead to an experimental evaluation of the contribution of shape anisotropy to coercive force.

ACKNOWLEDGMENT

I wish to thank T. O. Paine for his many helpful suggestions and E. F. Fullam for his generous contribution to the taking of the electron micrographs.

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[9] L. Weil and S. Marfoure, Compt. rend. **225**, 229 (1947).
[10] L. Néel, Compt. rend. **224**, 1488 (1947).

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A New Permanent Magnet from Powdered Manganese Bismuthide

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BECAUSE the present demand for cobalt and nickel greatly exceeds their availability, there has been an increasing interest, both in this country and abroad, in the development of permanent magnets not containing these elements. The Magnetics Division of the Naval Ordnance Laboratory, as part of its program of developing improved and nonstrategic magnetic materials for military and industrial use, has developed bismanol, a new high energy product permanent magnet. This magnet was prepared by hot-pressing the finely pulverized anisotropic intermetallic compound, manganese bismuthide (MnBi). A typical demagnetization curve for bismanol is illustrated in Fig. 1, which shows a maximum energy product $(BH)_{max}$ of 4.3×10^6 gauss-oersteds, a coercive force (H_c) of 3400 oersteds, and a residual flux density (B_r) of 4300 gauss. That this was possible was first predicted by Guillaud[1] as early as 1939. Guillaud, in

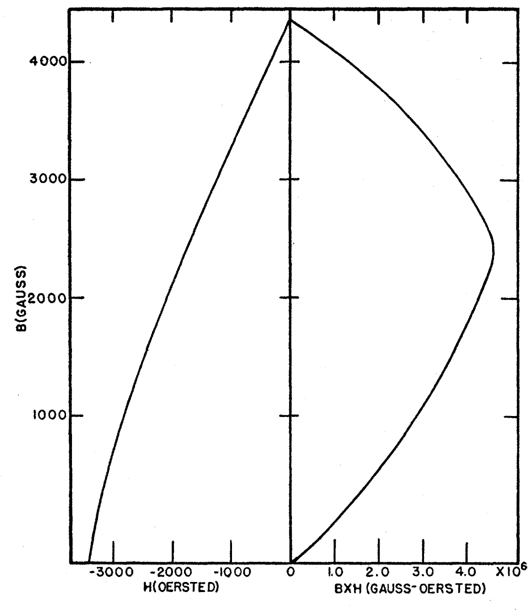

FIG. 1. Demagnetization and energy product curves—bismanol.

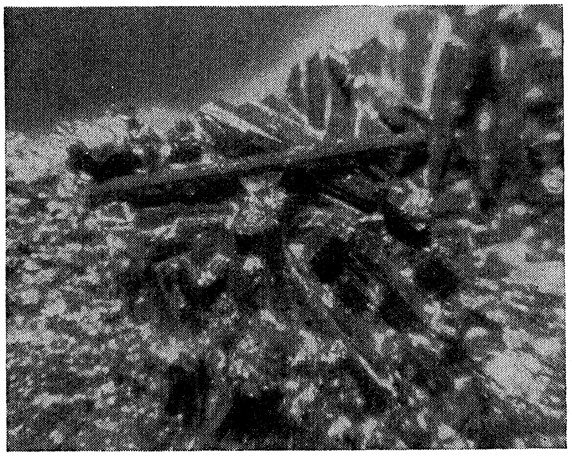

FIG. 2. Hexagonal crystals of MnBi.

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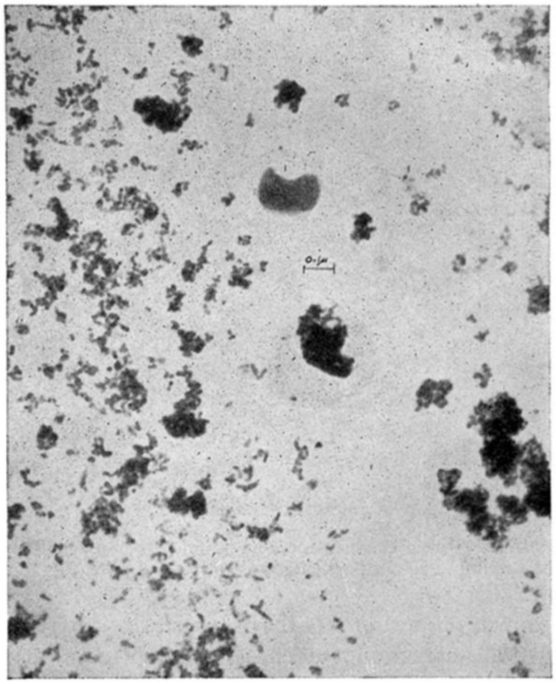
[1] C. Guillaud, thesis, University of Strasbourg (Strasbourg, France), 1943.



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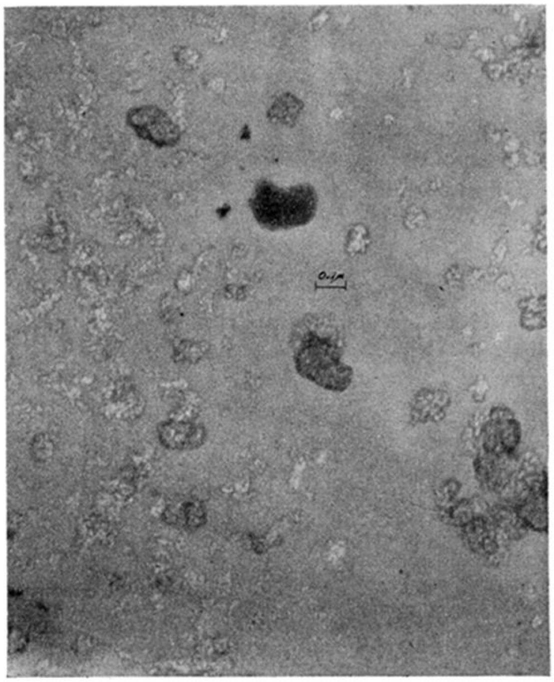
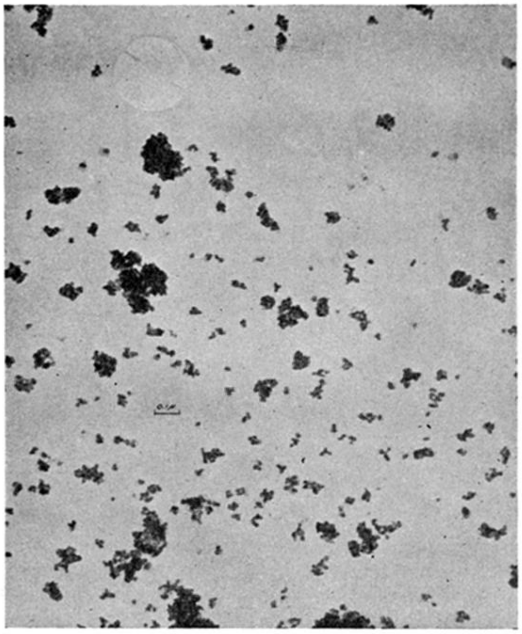


FIG. 3. Electron micrograph of same area as Fig. 2 after dissolving the iron particles to form a cavity. Some particles that have not been dissolved can be used as size reference.



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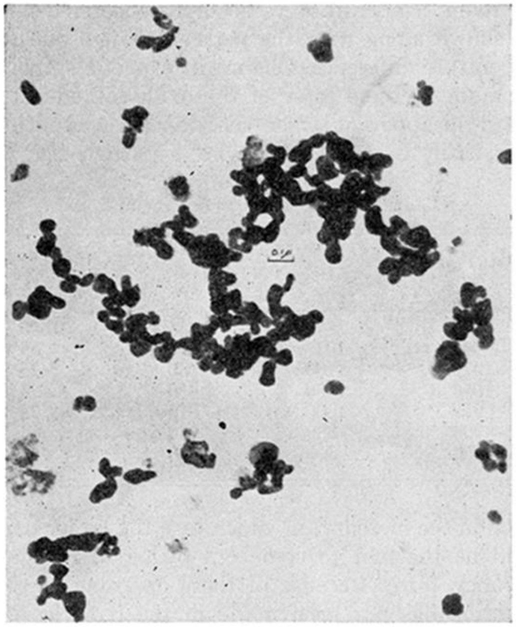

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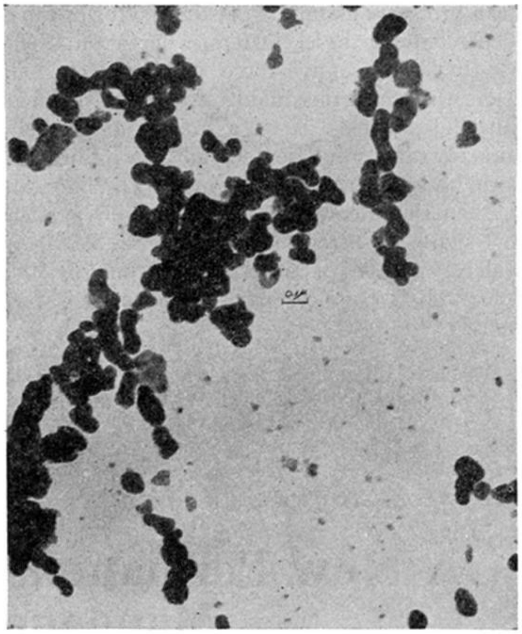

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