

Technical Report

TR44.0036
February 9, 1968
IBM Confidential

IBM Systems Development Division, Boulder Laboratory

NEW MAGNETIC PARTIC
DIGITAL RECORDING S

G. Bate

NEW MAGNETIC PARTICLES FOR
DIGITAL RECORDING SURFACES

G. Bate

ABSTRACT

The report discusses the magnetic properties of particles that should be considered as possible successors to the γ -Fe₂O₃ particles currently used in magnetic tapes and discs. The materials covered include cobalt-doped γ -Fe₂O₃, chromium dioxide, and metal particles.

The report concludes that, if the time required to develop a successful coating were not a factor, the most promising particles would be the G. E. "Lodex" metal particles (first choice) or the Sony "Hi-D" metal particles (second choice). If time is an important factor, so that a binder system is needed which is similar to the systems now in use, then the chromium dioxide or the 3M "High-Energy" particles would be a good choice.

The use of these particles having magnetic properties superior to those of conventional γ -Fe₂O₃ can only lead to the achievement of reliable recording performance at higher densities and data rates.

Descriptors:	Particles	Pyrophoricity
	Magnetic properties	Coatings
	Iron oxide	Tapes
	Cobalt-doped iron oxide	Discs
	Chromium dioxide	Storage density
	Metal particles	Coercivity
	Temperature dependence of magnetic properties	Remanence

IBM Confidential

This document contains information of a proprietary nature. ALL INFORMATION CONTAINED HEREIN SHALL BE KEPT IN CONFIDENCE. None of this information shall be divulged to persons other than: IBM employees authorized by the nature of their duties to receive such information, or individuals or organizations authorized by the Systems Development Division in accordance with existing policy regarding release of company information.



INTRODUCTION

During the summer and fall of 1965 the author wrote a book section on "Materials for Magnetic Recording." The manuscript was subsequently published as an IBM Technical Report.¹ It now seems appropriate to have a more up-to-date and less encyclopedic discussion of those magnetic particles which show the greatest promise for use in future digital recording surfaces. Since this report is not intended for outside publication, it is possible to consider factors such as compatibility and availability of the particles and, more important, to make recommendations.

It should be stressed at the outset that it is the magnetic properties of the particles which will receive the most attention in this report. This is not because the other problems, e. g. coatability, tape and head wear, etc., are not important, but simply because other people are much better informed on these topics and more competent to discuss them than is the author.

As the title suggests, the report contains no discussion of thin metallic films as recording surfaces. A reasonably up-to-date survey of these surfaces is given in the report previously referred to.

It is appropriate at the outset to discuss whether any new particles are needed; i. e., what do we know about the ultimate capability of thin recording surfaces (30-50 microinches) of γ -Fe₂O₃? The answer is, "Not very much." We must remember that the recording material is only one link in the information storage chain, the others being coating thickness, roughness, tape-to-head separation, head gap length, etc., etc. Consequently it is very difficult to predict the ultimate performance before the expected improvements in the other parameters have been obtained and their implications studied. What we can say at this time is that increases in coercivity and remanence and decreases in particle size in conjunction with the other improvements can lead to no other result than the achievement of reliable recording at higher densities and data rates even for thick (i. e., 500 - microinch) tapes.

THE SIGNIFICANT MAGNETIC AND
PHYSICAL PARAMETERS

The relevant fundamental properties of the magnetic particles are:

- 1) The saturation intensity of magnetization.
- 2) The magnetic anisotropies.
- 3) The shape and size.

Since it is usually easier to measure a known mass than a known volume of material, the saturation intensity of magnetization per unit mass, σ_s , is commonly quoted, the units being emu/gm. This quantity is a measure of the maximum magnetization of the material and is clearly related to the maximum magnetic flux obtainable. The magnetic anisotropies are (a) shape anisotropy, (b) magnetocrystalline anisotropy, and (c) magnetoelastic anisotropy. For the materials of interest here (c) will not be mentioned further. The remaining two anisotropies, separately or in concert, determine the fields needed to reverse the particle magnetization. The most common of these fields is the coercivity H_c , but there are other critical fields of significance. These are:

- H_r , the field required to reduce the remanence to zero.
- H_{rs} , the field required to produce maximum remanence (related to the "saturation" writing current).
- H_a , the maximum anisotropy field--the field required to switch the "hardest" particles in an assembly.

The precise connection between these anisotropies and the coercivity (say) is as yet imperfectly understood because the mechanism of magnetization reversal in the particles is not properly understood, and we often talk of "the coercivity of a particle assembly" as if it were a fundamental property. It is not; but it is controlled by the fundamental quantities, by the dispersion and orientation, and it is easily measurable.

For magnetic recording application we need particles whose size is in the single-domain region. If the size is too great there is a possibility of magnetization reversal by domain-wall motion. This is a relatively low-energy process and leads to low coercivities. If the size becomes too small, then the particles lose their ferromagnetism and become superparamagnetic. The boundaries of the desired single-domain behavior depend somewhat on the other fundamental properties and shape but can be roughly given as 0.01 to 1.0 microns.

As high-density recording surfaces are pre-eminently thin surfaces of high coercivity, the trend will be toward smaller particles. Since we never deal with a uniform particle size and shape but always with a distribution, there will be an increasing danger that more and more of the smaller particles in a distribution will be below the lower critical size for single-domain behavior. Particles below this limit will not contribute to the information storage process.

The fundamental particle properties then determine the following practically interesting properties, which are listed in probable order of importance in the recording process: coercivity H_c , remanent intensity of magnetization $*I_r$, I_r/I_s , sH_r , $\left. \frac{dI}{dH} \right)_{H=H_c}$, H_r . The remaining physical parameter is coating thickness t , which is at least of equal importance with the coercivity. In high density digital recording we require that the signal pulse obtained from each bit have an amplitude high enough to make it clearly identifiable above the system noise. Also we require that the pulses should be narrow so that pulse interference is minimized. According to our present understanding pulse amplitude is $\propto \sqrt{H_c I_r t}$ and pulse width $\propto \sqrt{t/H_c}$; thus high coercivities are advantageous for both amplitude and width, with the ultimate limit being imposed by the ability of the heads to write and to erase the surface. Since the narrowness of a pulse is generally more important than the height of the pulse we prefer that the coating thickness t should be small, ($\ll 100$ microinches and preferably < 50 microinches).

The remanent intensity I_r depends on the fundamental property I_s (or σ_s), on the anisotropies, and on the degree of particle orientation. Particles which rely on magnetocrystalline anisotropy for their magnetic hardness generally have six or eight equivalent easy directions of magnetization, whereas shape-anisotropic particles usually have just two equivalent directions. Both types of particle may be oriented in a magnetic field, but the reward in terms of increased remanence over that of a random particle array is higher for the shape-anisotropic particles.

To sum up, for high density digital storage we need particles that are small (largest dimension \ll coating thickness), that have high coercivity (400 to 750 oe), and that have a high value of saturation magnetization (σ_s). These are by no means the only relevant properties, nor does possession of these properties guarantee that a superior recording surface can be made from the particles. The properties merely indicate the first set of questions which we should ask about new particles before they can be given further consideration.

The table lists these and other properties for a limited number of different particles which seem at this time to offer the best hope for improved digital recording surfaces. The properties of conventional γ - Fe_2O_3 particles are also included for purposes of comparison. The table lists the composition of the particle material, its source, the particle shape, and the normal range of the particle size, together with the magnetic properties σ_s , H_c , the Curie temperature θ_c , and the dominant magnetic anisotropy, i. e., the principal reason for the high coercivity exhibited by the particles.

$$*I = \frac{\text{Magnetic Moment, M}}{\text{Sample Volume, V}}, \quad \sigma = \frac{\text{Magnetic Moment, M}}{\text{Sample Mass, m}}$$

$$\text{thus } I_r/I_s = M_r/M_s = \sigma_r/\sigma_s.$$

PARTICLE MATERIAL	SOURCE	PARTICLE SHAPE AND SIZE	σ_s (e. m. u./gm)	H_c (oersteds)	θ_c (°C)	DOMINANT ANISOTROPY
<u>γ-Fe₂O₃</u> IRN 110 (IBM tape)	Pfizer	Acicular l = 0.3 μ - 1.0 μ w = 0.1 μ	70 - 74	275-300	590	Shape
	Pfizer	Acicular l = 0.2 μ w = 0.03 μ	70 - 74	285-305	590	Shape
<u>Doped Iron Oxides</u> 3% Co-substituted γ -Fe ₂ O ₃ EX-1312	Pfizer	Cubic l = 0.05 μ	45 - 55	515-555		Magneto-crystalline
	3M	Acicular l = 0.2 to 0.7 μ w = 0.05 μ	\sim 100 (estimated) \sim 67 (measured)	350		Shape and magneto-crystalline (Note: H_c values as 900 oe are claimed for this materials presumably by changing doping level.)
<u>Cr₂O₃</u> + \sim 2% (wt) Sb ₂ O ₃ (catalyst)	DuPont	Acicular l = 0.05 - 0.4 μ 2 = 0.03 μ	79	350-500 (higher coercivities obtainable)	126	Shape
	Matsushita	Acicular l = 0.05 - 0.4 μ w = 0.025 μ	σ 3000oe, 20°=72 σ_{∞} , 20° = 105	350-600	126	Shape
<u>Metals</u> Fe 55 - 60% Co 30 - 35% O 15 - 5% by electrodeposition into Hg cathode and coated with oxide. (modified "Lodex" particles)	G. E. --	Acicular l = 0.014-0.12 μ w = 0.010-0.02 μ	160-210	200-2000	> 950°C	Shape
	Computron					
	Chevron Research Co.	Spherical dia = 0.02 μ	150-160	200-900	1070	Shape ("chain-of-spheres")
	Sony	Spheroidal dia \sim 0.05 μ	150-200	500-900	\sim 900	Shape (possibly "chain-of-spheres")
	DuPont	Acicular l = 0.05 - 4 μ w = 0.01 - 0.1 μ	100-160	100-1500	\sim 800 (estimated)	Shape
<u>Cobalt</u> by decomposition of Co ₂ (CO) ₈						
<u>Fe - Co</u> 37.5% Fe, 62.5% Co ("Hi-D") reduction of oxalate						
<u>Fe-O-B</u> 82 - 98% Fe 0.5 - 15% O 14 - 3% B Ferric chloride and sodium borohydride in a magnetic field						
<u>Fe-whiskers</u> by vacuum deposition	G. E.	Cylindrical dia: 250 Å to 1100 Å	222 (estimated)	2,800 300	770	Shape

TABLE
PROPERTIES OF SOME MAGNETIC PARTICLES

COMMENTS ON THE MATERIALS
COVERED IN THE TABLE

The Curie temperatures for the cobalt-doped iron oxide are not known. The temperature-sensitive properties² of these and other materials will be discussed later. There is some question about the value of σ_s for 3M's "High-Energy" particles: the values reported³ by 3M imply that $\sigma_s \sim 100$, whereas IBM Boulder's measurements on oxide extracted from tape give $\sigma_s \sim 67$.

One property of the chromium dioxide⁴ particles which does not emerge from the table is their high dispersibility and orientability. This is probably attributable to the smooth dendrite-free surface of these particles. In order to reduce the reaction temperatures and pressures an oxide catalyst (ruthenium, antimony, or tellurium) is added. The catalyst finds its way into the finished particles and is said to result in smaller, more acicular particles.

Measurements on σ_s by J. K. Alstad and A. Grady (Boulder) reveal a value of 72 at 20°C and a field of 3000 oe; the value on extrapolation to infinite fields is 105 emu/gm.

Luborsky⁵ has described the basic steps whereby elongated single-domain (E. S. D.) particles of iron or iron-cobalt can be produced by electrodeposition into a mercury cathode. These particles are presently being made into magnets which are sold under the tradename LODEX. A modification of this process which resulted in particles of Fe-Co enclosed in a sheath of the oxide was described by Falk.^{6,7,8,9} This sheath not only serves to protect the particles but also gives greater coercivity than that of Fe-Co (LODEX) particles as a result of the exchange anisotropy from the metal-oxide interface.

The cobalt particles^{10, 11} produced by the decomposition of cobalt carbonyl are almost spherical and are of very uniform size. The spheres form long (length \gg particle diameter) chains which can be oriented in a magnetic field. The particles are coated with a polymer at the time of their formation and this serves to protect them from oxidation.

The Sony (Hi-D) particles are made by the reduction in hydrogen of a metallic oxalate prepared from a mixture of iron and cobalt chlorides (4:6) with oxalic acid.¹² Apparently it is difficult to produce particles reproducibly (and of high I_r/I_s) with a coercivity less than about 500 oe by this process.

A novel process for preparing non-pyrophoric ferromagnetic particles was described by Miller and Opegard¹³ (du Pont). Iron or iron and cobalt salts are mixed with sodium borohydride in the presence of a magnetic field ($H \sim 5,000$ oe), and a black precipitate of ferromagnetic particles is obtained directly.

Finally, Morelock¹⁴ and Luborsky¹⁵ describe a method for preparing iron whiskers of very high purity and very small diameter (100 - 1000 Å) from an atmosphere of the supersaturated metal vapor at a pressure of 10^{-6} mm Hg and a temperature of 1100°C. Since the preparation method is physical rather than chemical, the process is presumably more controllable than the methods described above. Protection of such fine whiskers from oxidation would, however, present a problem.

4

TEMPERATURE-SENSITIVE MAGNETIC PROPERTIES

Two temperature-dependent magnetic properties must be considered. First, all ferro- and ferrimagnetic materials treated here exhibit a reduction in σ_s as the temperature is increased from room temperature to the Curie temperature θ_c . This leads not only to a reduction in the external flux but also a reduction in the demagnetizing field ($H_D = N'\sigma$, where N' is determined by the bit geometry). In those particles deriving their magnetic hardness from shape anisotropy, the coercivity is also proportional to σ , and thus we have the situation that the driving force which leads to broad pulses (the demagnetizing field) and the factor describing the ability to resist demagnetization (the coercivity) both decrease at the same rate. Thus although we must expect the signal output pulses obtained from these materials to decrease in amplitude as $T \rightarrow \theta_c$, on cooling to room temperature the original amplitude should be regained and no permanent loss of stored information suffered (assuming $T_{\max} < \theta_c$). This temperature-dependence would be shown by recording surfaces made of CrO_2 whose $\theta_c = 126^\circ\text{C}$. For all other acicular materials in the table the Curie temperature is so high as not to be a problem.

The second type of temperature dependence is more serious. In materials whose dominant anisotropy is magnetocrystalline, the coercivity is given by an expression of the form $H_c = 2K/I_s$, where K is the anisotropy constant and I_s is the saturation magnetization/unit vol. It usually happens that K is very temperature-sensitive and, although I_s decreases with increasing temperature, K decreases much more rapidly. Thus the ability to withstand demagnetization decreases more quickly than does the demagnetizing field ($H=NI$), and information is permanently lost when the temperature is increased.¹⁶ This type of temperature sensitivity is encountered in, for example, the cobalt-doped $\gamma\text{-Fe}_2\text{O}_3$ particles.

It should be remarked here that merely making the particle acicular does not eliminate this temperature dependence. We then have the case of two anisotropies--shape and magnetocrystalline--acting at the same time, and the latter component can still show a sensitivity to changes in temperature. If the structure of the particle is such that the long axis of the particle coincides with one of the preferred crystallographic axes, then the two anisotropies will cooperate and the coercivity will be larger than if either anisotropy were operating singly. This situation is probably

found in the 3M "High-Energy" particles. These particles contain 3.6% Co and 3.7% Mn and show a temperature dependence of coercivity comparable with that of a non-acicular 2% Co sample.¹⁷

OTHER PERTINENT FACTORS

5.1. PARTICLE AVAILABILITY

Clearly, even the particles which are most appropriate from a purely magnetic point of view would be of little practical use if a cheap, reliable method of preparing them in large quantities were not available. Thus it is very appropriate to comment briefly on this point for each of the particles (except ordinary γ - Fe₂O₃).

5.1.1. Doped Iron Oxides. Particles of EX 1312 are available in quantity from Pfizer at a price of \$2.75 a pound for 150 pounds (cf. 0.50¢ a pound for ordinary γ - Fe₂O₃).

At this time 3M Corporate Management has not revealed whether or not the Company will supply "High-Energy" (cobalt, manganese doped γ - Fe₂O₃) particles. The Company has said that the manufacturing process involves the same equipment as is used for their conventional γ - Fe₂O₃ particles, and so we might expect that if the particles are sold the price will be similar to that of Pfizer EX 1312 particles, i. e., \$2.75 a pound.

5.1.2. Chromium Dioxide. Chromium dioxide particles prepared by du Pont are not available to IBM. Particles of this material made by Matsushita are available at a cost of about \$50.00 a pound for small quantities.

5.1.3. Metal Particles. The G. E. - Computron (LODEX) particles are available at a cost of \$100 a pound for 1-pound lots; the iron whiskers are not commercially available.

The Chevron Research Company is no longer making the spherical cobalt particles, but the Company has no objection to IBM's attempting to make the particles by their process. The highly toxic nature of carbonyls would appear to be a practical disadvantage of this process.

Sony presently use their "Hi-D" particles in master audio recording tapes, in the laboratory in magnetic transfer tapes, and in a speed control mechanism on tape-drive capstans. The estimated price of the particles (L. G. Taft) is \$5 - 10 a pound.

Du Pont is not known to be making the particles of Fe-O-B and nothing is known of their availability.

Thus about half the particles in the table (Pfizer EX 1312, Sony Hi-D, G. E. Lodex, and Matsushita CrO₂, and possibly the 3M "High-Energy" particles) are available commercially at prices ranging from \$2.75 to \$100 a pound. It is to be expected that the high "small lot" prices would be substantially reduced by large-scale particle production. A 2400-foot reel of 500-microinch-thick computer tape contains about 1/3 pound of magnetic material, and this amount would of course be still lower in thinner coatings. Thus while prices up to \$5 a pound would not have a major effect on the selling price of tape, the same cannot be said for the Lodex particles at the present price.

5.2. COATABILITY AND LOADING

After a magnetic particle has been manufactured and shown to have magnetic properties appropriate to high density recording surfaces, there begins the complex task of finding a suitable binder system. The system must be such that it allows the particles to be dispersed at an adequate loading (volume packing fraction), oriented if necessary, and bound to the substrate in a medium of such physical properties that recording surface wear and head wear are minimized. As the magnetic particles become smaller it is more difficult to maintain even the present particle loading of 40% (by volume) since the ratio of surface area to volume increases with decreasing particle size and proportionately more binder material is needed to encapsulate a particle.

This difficult question of organic-physical-inorganic chemistry will not be discussed further here; it is better left to a coating--or a surface--chemist.

5.3. PYROPHORICITY OF METAL PARTICLES

One practical disadvantage which is common to small metal particles is that they are liable to burn spontaneously on exposure to the atmosphere unless measures are taken to protect them. The rate of oxidation increases with the surface area of the particles, while the temperature increase associated with the heat of oxidation varies inversely as the particle volume. Thus it is expected (and found) that the pyrophoricity of the metal particles depends critically on their surface area-to-volume ratio. That is, acicular particles or, more especially, porous particles are more pyrophoric than, say, solid spherical particles. To a second order, we might expect that pyrophoricity also depends on the chemical activity of the element, so that iron would be more pyrophoric than cobalt, and cobalt more than nickel.

In general, all metal particles of diameter less than about 0.5μ must be treated with caution. There are two principal methods of overcoming the problem. The first of these, employed in the preparation of the Chevron cobalt particles, consists of applying a suitable plastic overcoat to the particles so that the reactive surface of the metal is shielded from the air. The second method is to allow air to reach the particles slowly and controllably so that a thin protective film of oxide is formed on the particle surface. This may conveniently be achieved by keeping the particles under a liquid such as benzene or toluene so that the oxygen must diffuse

through the liquid in order to reach the particles. When it is required to coat the particles onto a recording surface, the protective liquid is replaced by the solvent-binder mixture. However, even after the coating has dried, there is the possibility with some binder compositions that air may diffuse in and oxidize the particles or that the protective coating may be abraded away. The published literature on this subject is extremely sparse.

6

THE QUESTION OF COMPATIBILITY

The task of describing a superior high density recording surface which is compatible with present tapes (say) and usable on present drives without modification invariably presents a serious problem. The trend, as we have seen, is in the direction of materials having increased coercivity and remanent intensity. But increasing the coercivity may make the writing and erasing fields insufficient unless the writing and erasing currents are increased. A simultaneous reduction in the coating thickness (or, more exactly, the recording depth) could perhaps be made to compensate for the increase in coercivity to some extent.

On the other hand, if the remanent moment is increased the signal output will also increase and saturation of the existing signal amplifiers can become a problem, particularly with high-output heads and high recording densities. There are already indications that the du Pont "Crolyn" (CrO_2) tape, which is said to be IBM compatible at 800 bpi (and is indeed found to be compatible at this density), gives an output at 1600 bpi which would saturate the amplifiers on those drives in which the head output was at the upper end of the specification.

Thus the constraints (of limited coercivity and limited remanence) may be so restrictive that it is impractical to make those changes which would lead to a truly superior half-inch tape, i. e., one with large pulse amplitude and small pulse width. It is probably not much of an exaggeration to say that the only recording surface which is really compatible with half-inch γ - Fe_2O_3 tape is half-inch γ - Fe_2O_3 tape!

Clearly we may have to change something in the half-inch tape drives, e. g. the write/erase current and/or the signal amplifiers, if we want to derive any benefits from the new materials. These benefits include greater signal amplitude at present recording densities, or operation at higher densities, or both. Reduction of the tape manufacturing costs is specifically not one of the expected benefits unless it should happen that a new particle enables a binder system which is cheaper (i. e. simpler, of higher yield) to be employed.

The principal roles for the new particles must be in new recording devices such as Cybernet or the new disc files, which are not required to use both new and old materials.

CONCLUSIONS AND RECOMMENDATIONS

If time and the pressing needs of product programs were not factors in the choice, then the most promising particles for future recording surfaces are the metal particles, and of these particles the G. E. "Lodex" (first choice) and the Sony "Hi-D" (second choice) are the most attractive.

Neither would enable recording surfaces to be made of high-density potential equal to that of thin (5 - 10 microinch) metallic films, however.

The "Lodex" particles are to be preferred over the "Hi-D" particles, principally because I feel that G. E. has much more control over their magnetic properties, particularly for particles of $H_c \lesssim 500$ oe. This results from their fifteen years of experience in developing the particles.

The reason that time becomes an important factor in these recommendations is that much more is known about the coating properties of non-metallic particles (e. g. , γ - Fe_2O_3). Since the time needed to develop a suitable binder for a metal particle may be considerable, a conservative choice for a particle which could presumably be incorporated successfully into a superior tape or disc in 1 1/2 to 2 years would be either the Matsushita CrO_2 or the 3M "High-Energy" material.

CrO_2 is to be preferred since we do not know at this time whether the "High-Energy" material will be made available to us as particles. Very recent experiments in our laboratory on the decrease in signal amplitude (after storing at different temperatures) of pre-recorded tapes of CrO_2 and 3M "High-Energy" particles have shown little difference for storage temperatures of $16^\circ C$ to $100^\circ C$. The tape samples were stored for one hour at each temperature. "All-ones" patterns at densities of 500 to 4000 fri were written, and the decreases in signal amplitudes at the two extreme densities were:

	<u>500 fri</u>	<u>4000 fri</u>
CrO_2	28%	33%
"High-Energy"	22%	35%

Rather than obtaining particles from other manufacturers, it may be preferable, from considerations of cost, freedom to "design" particles for a specific need, surety of supply, and, last but not least, prestige, for IBM to develop and manufacture its own particles. In this event metal particles should be the target, on the basis of their promise and our previous development experience.

Finally, it should be recognized that obtaining particles having desirable magnetic properties is only one aspect, and probably a relatively minor aspect, of the total job. The difficult, time-consuming, complex, and interrelated questions of surface chemistry, polymer chemistry, rheology, and wear can really begin only at the point where "magnetic" development ends.

ACKNOWLEDGMENT

It is a pleasure to acknowledge the considerable help which the author has received from his colleagues: J. K. Alstad, T. J. Beaulieu, M. A. Every, A. Grady, R. S. Haines, J. E. Hurt, H. D. McCabe, G. E. Moore, C. C. Parker, R. S. Perzan, R. W. Polleys, C. S. Roark, R. E. Smith, and J. S. Vranka.

REFERENCES

1. G. Bate, Materials for Magnetic Recording, IBM Technical Report TR44.0015, Boulder, February 28, 1967. A rather lengthy account of a wide range of materials (both particulate and thin films) prepared for outside publication during the summer and fall of 1965.
2. D. E. Speliotis, J. R. Morrison, and G. Bate, Thermomagnetic Properties of Fine Particles of Cobalt-Substituted γ -Fe₂O₃, IBM Technical Report TR00.1233, Poughkeepsie, December 21, 1964. Compares the temperature-sensitive properties of Pfizer EX-1312 powder with those of conventional γ -Fe₂O₃ particles.
3. C. S. Roark, File Memorandum on Meeting with 3M, December 29, 1967. Disclosure by 3M of their "High-Energy" tape.
4. F. J. Darnell, Journal of Applied Physics **32**, 1269 (1961). Survey of the magnetic properties of chromium dioxide particles.
5. F. E. Luborsky, Journal of Applied Physics **32**, 171S (1961). Review of the preparation and properties of elongated single-domain (E. S. D.) particles of Fe-Co.
- *6. R. B. Falk, U. S. Patent 3,156,650, November 10, 1964.
- *7. R. B. Falk and G. D. Hopper, Journal of Applied Physics **32**, 190S (1961).
- *8. R. B. Falk, U. S. Patent 3,198,717, August 3, 1965.
- *9. R. B. Falk, U. S. Patent 3,262,812, July 26, 1966.
- **10. J. R. Thomas, Journal of Applied Physics **37**, 2914 (1966).
- **11. O. L. Harle and J. R. Thomas, U. S. Patent 3,228,882, January 11, 1966.
12. B. Leland, Technical notes on visit to Sony, August 1965.
13. H. C. Miller and A. L. Opegard, U. S. Patent 3,206,338, September 14, 1965. Describes the preparation and properties of Fe-O-B particles prepared by the reaction of iron and cobalt salts and sodium borohydride in a magnetic field.

* Iron-cobalt particles with oxide coating.

** Cobalt particles by decomposition of Co₂ (CO)₈.

- ***14. C. R. Morelock, Acta Metallurgica 10, 161 (1962).
- ***15. F. E. Luborsky and C. R. Morelock, U. S. Patent 3,132,022, May 5, 1964.
16. J. R. Morrison and D. E. Speliotis, Cobalt-Substituted γ -Fe₂O₃ as a High Density Recording Tape, IBM Technical Report TR00.1280, Poughkeepsie, June 4, 1965. Signal loss after heating recorded tapes is discussed.
17. A. Grady, "A Comparison of the Temperature Sensitivity of Magnetic Properties of Two Cobalt-Doped Iron Oxides," File Memorandum, January 15, 1968. Compares the Pfizer (non-acicular) and the 3M "High-Energy" (acicular) particles.
18. C. S. Roark, "Chrome Dioxide," File Memorandum, August 1, 1967.

*** Preparation of iron whiskers.

APPENDIX

Nine typical electron micrographs of the particle assemblies discussed above are shown in the following figures.



ONE MICRON

35,000x

IRN 135

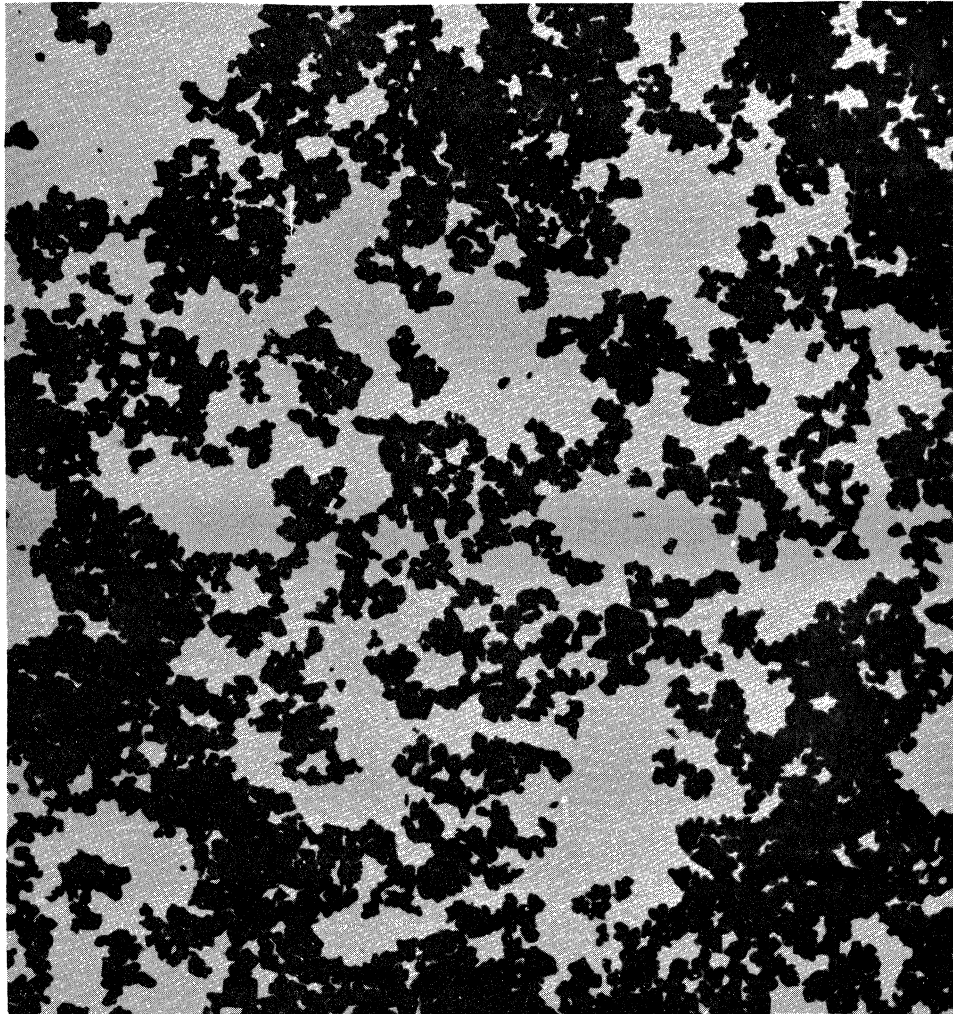
FIGURE 1

γ -Fe₂O₃ PARTICLES

Pfizer CX-5956 (new code MO-2350)

Used in IBM disc coatings

(Photo by Pfizer)



ONE MICRON

35,000x

EX 1312

FIGURE 2

COBALT-DOPED γ -Fe₂O₃ PARTICLES

Pfizer EX-1312 (new code MO-9853)
(Photo by Pfizer)



FIGURE 3
DU PONT CrO_2 PARTICLES
Photo by H. D. McCabe, SDD Boulder

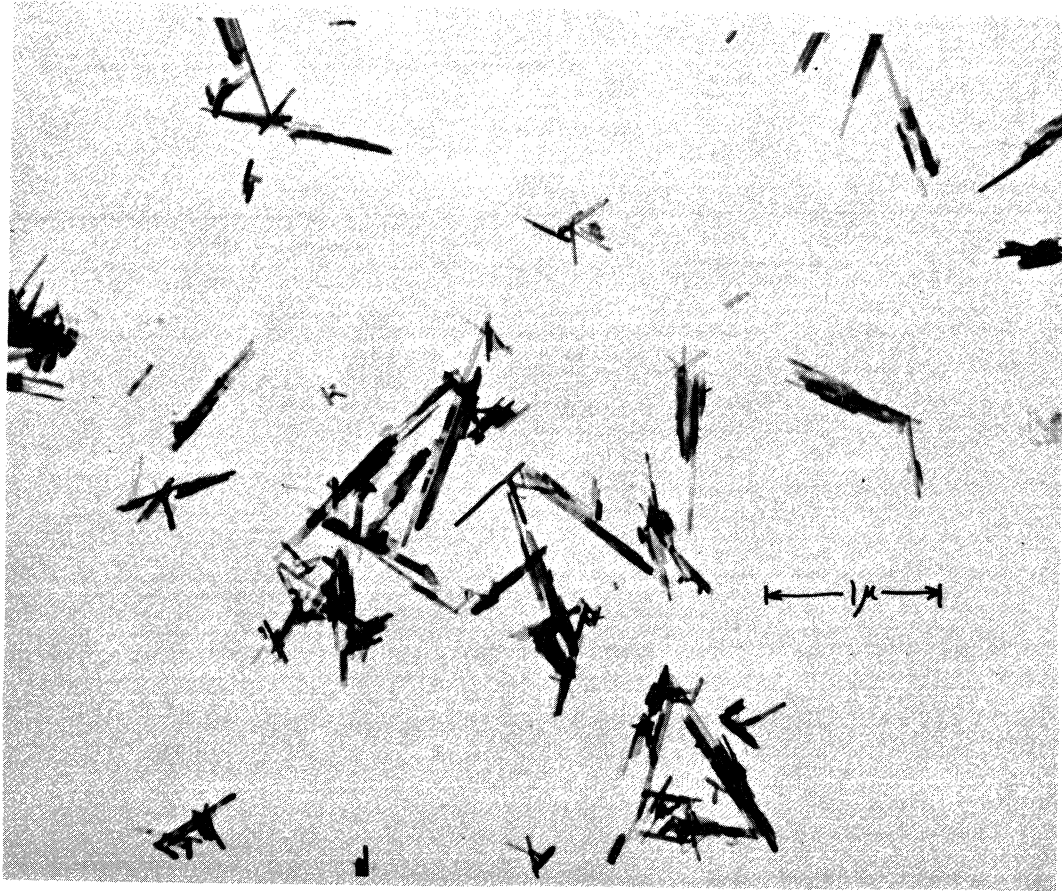


FIGURE 4

MATSUSHITA CrO_2 PARTICLES

Photo by H. D. McCabe, SDD Boulder



FIGURE 5

3M "HIGH-ENERGY" PARTICLES

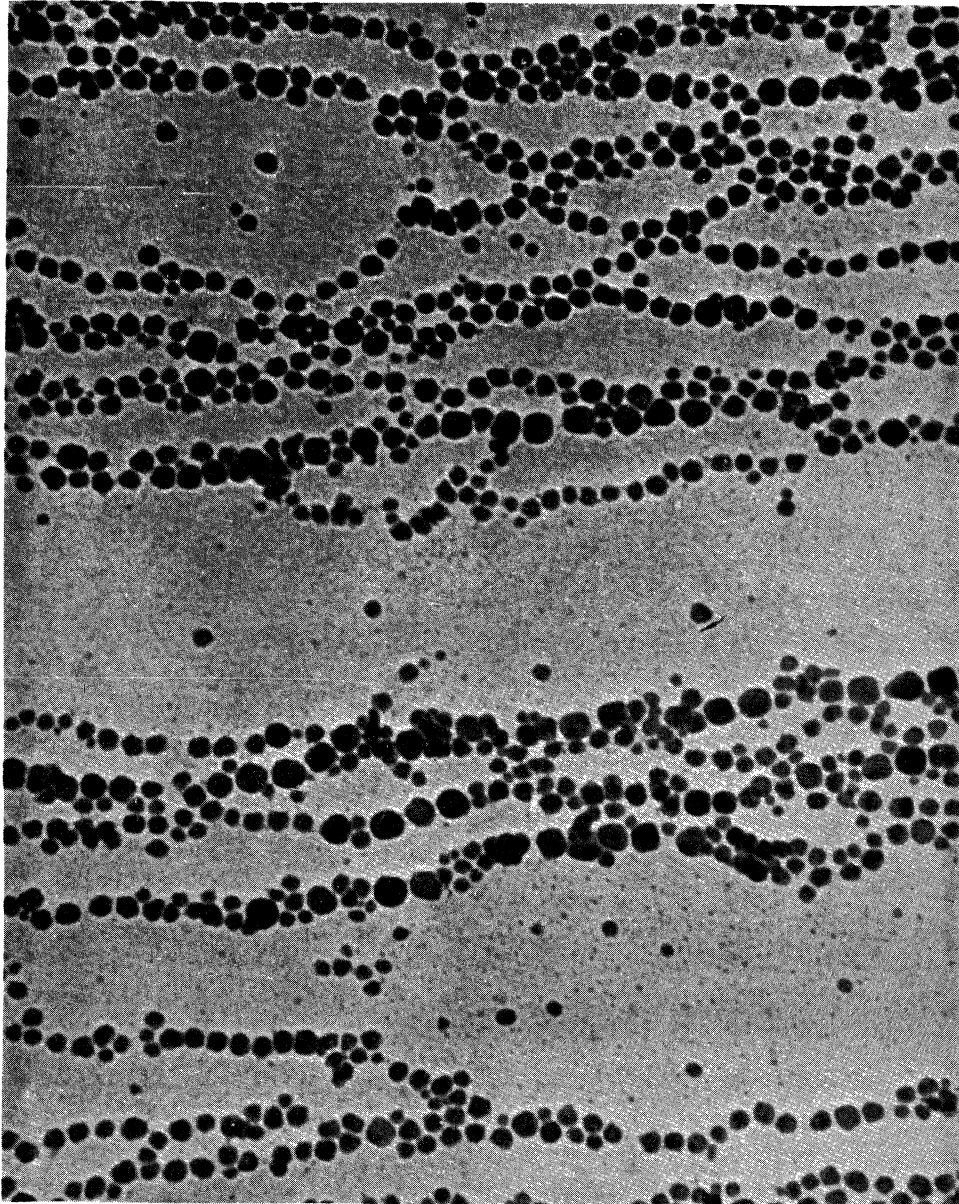
Particles extracted from tape by R. S. Haines and
photographed by H. D. McCabe, SDD Boulder.



FIGURE 6

GE "LODEX" Fe-Co PARTICLES

Photograph by courtesy of F. E. Luborsky, GE Research.



— $\frac{1}{10} \mu$ —

FIGURE 7

CHEVRON COBALT PARTICLES

Photograph by courtesy of J. R. Thomas, Chevron Research Company.

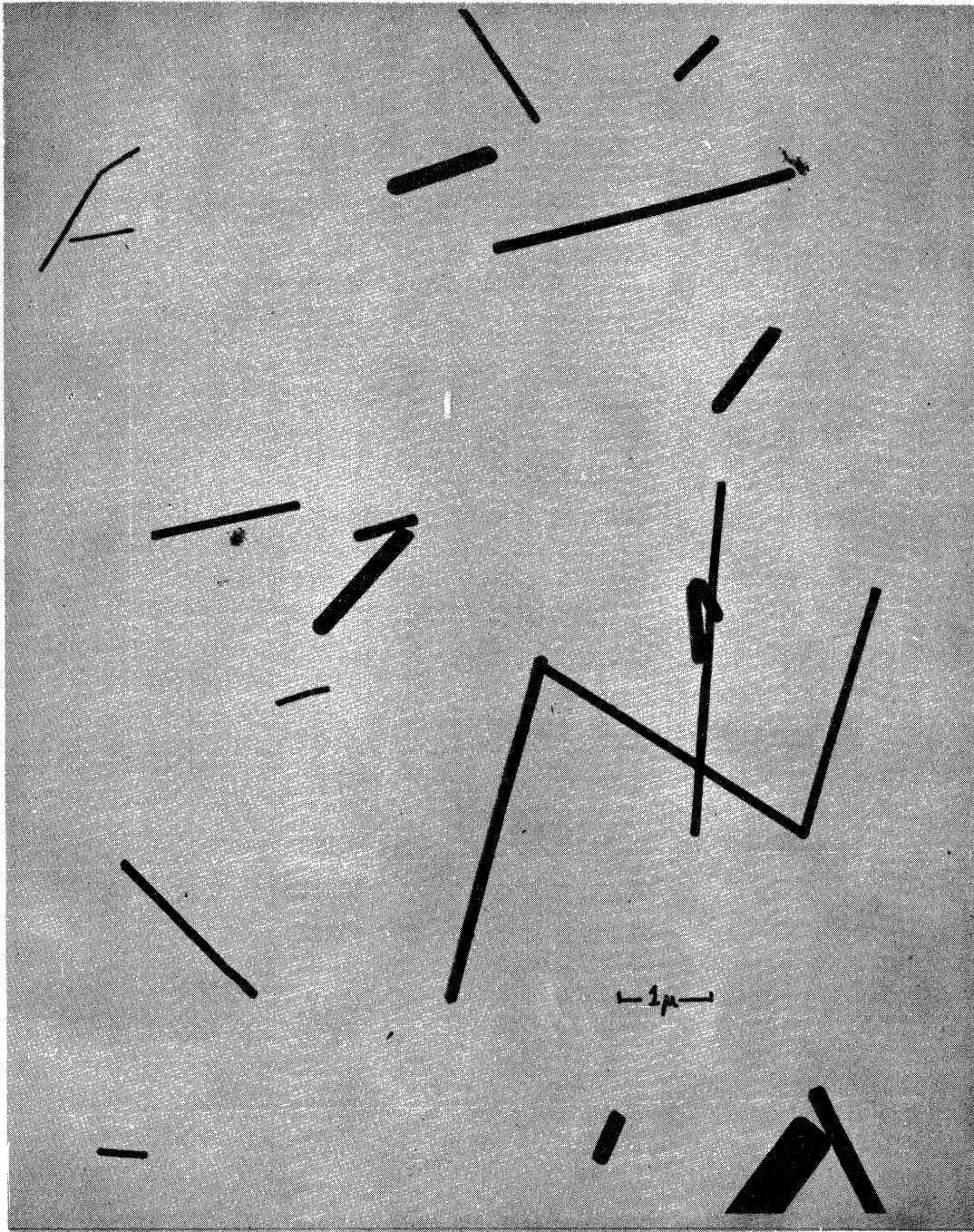


FIGURE 8

GE IRON WHISKERS

Photograph by courtesy of F. E. Luborsky, GE Research

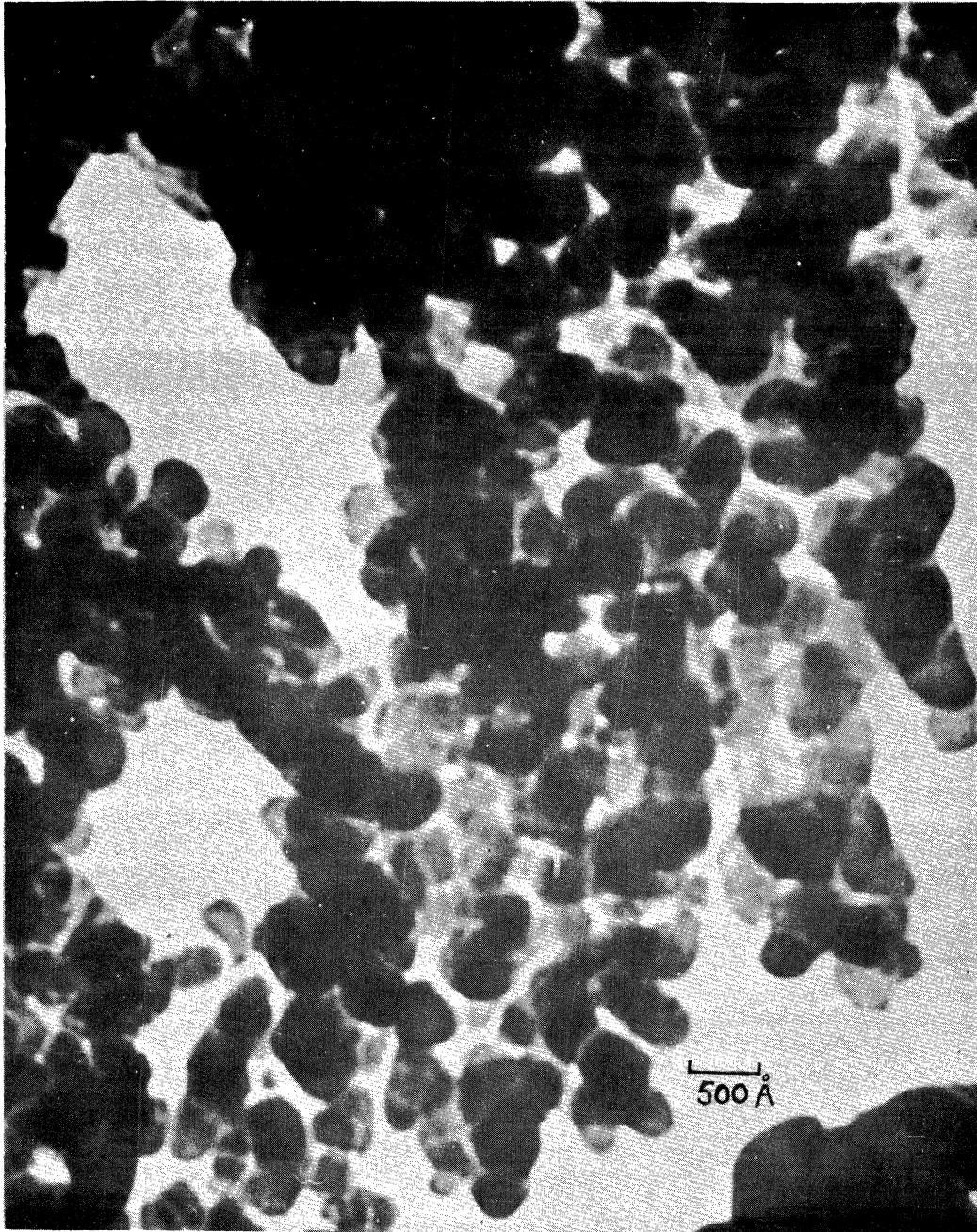


FIGURE 9

SONY "Hi-D" Fe-Co PARTICLES

Particles dispersed and photographed by H. D. McCabe,
SDD Boulder

