Magnetic Characterization Of Iron Oxide Dispersions

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Introduction

The most common magnetic particle used in tape coating is gamma ferric oxide, γ-Fe_2O_3. These are acicular particles with a length to width ratio of about six to one. During their production, agglomeration and sintering of the particles occur at the high temperatures required for conversion of alpha ferric oxide into gamma ferric oxide. The sintered particles and agglomerates must be properly broken up by shear forces imparted during the milling process. Particles of alpha ferric oxide, α-Fe_2O_3, are similar in shape to γ-Fe_2O_3 but are non-magnetic (or more correctly they are anti-ferromagnetic).

In this paper we address the effects associated with variations in γ-Fe_2O_3 (magnetic oxide) concentrations for Epoch-type formulated coatings. The response of each variation is also investigated as a function of dispersion/milling time. Results indicate that the presence of α-Fe_2O_3 in the formulation plays a definite role in the magnetic behavior of the coating. Examination of B-H loops for several oxide loading variations indicates an increase in squareness and orientation as the concentration of γ-Fe_2O_3 increases. Conversely, an increase in the α-Fe_2O_3 portion produces slightly higher coercivity values but also an undesirably high switching field distribution.

Experimental

Five γ-Fe_2O_3 concentrations were selected between 45 and 75% (based on total non-volatile formulation weight) as illustrated in Figure 1.

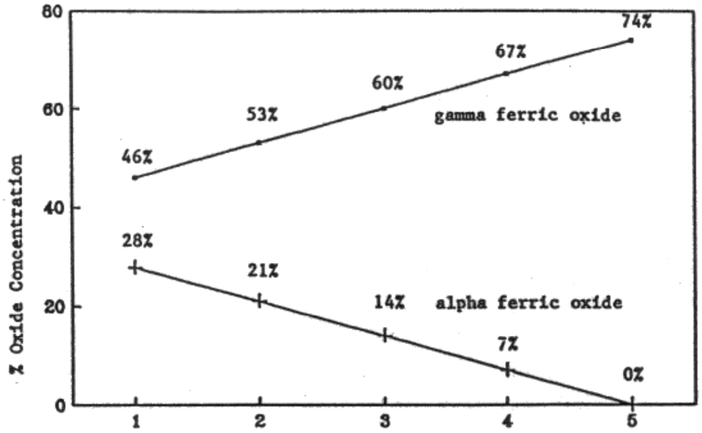


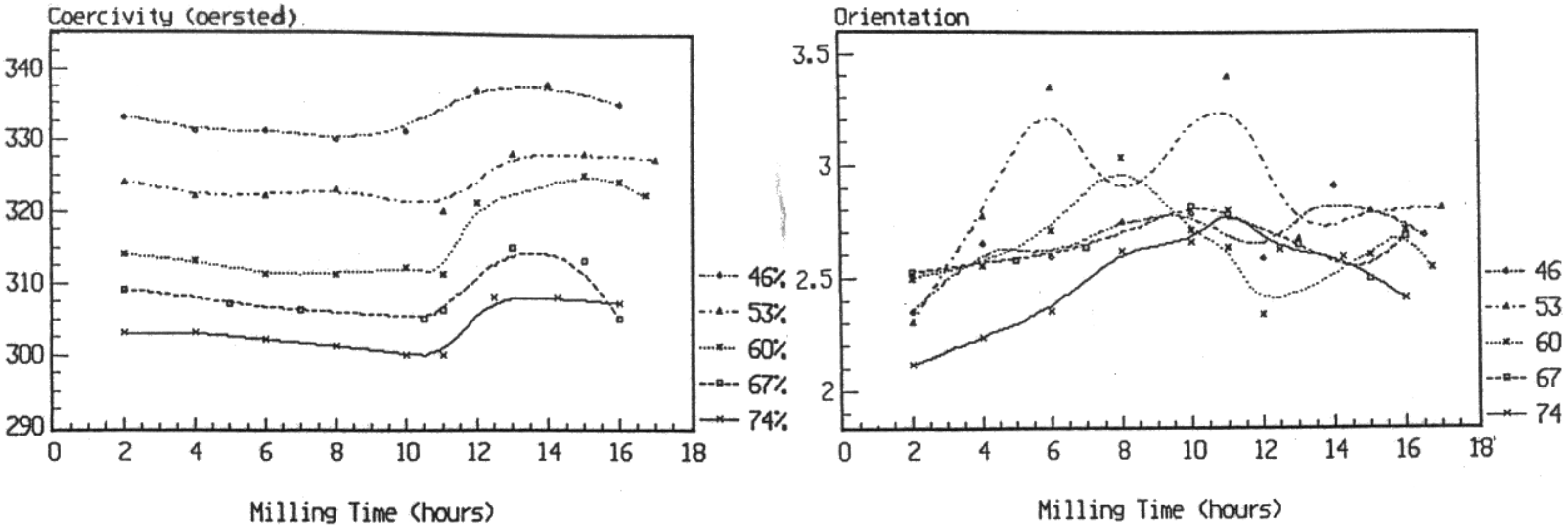
Figure 1. Preselected oxide loading concentrations

Standard Epoch formulations contain 65.5% of the gamma oxide and 6.5% of the alpha oxide. Each mill, formulated, processed and characterized separately, consisted of gamma and alpha ferric oxides, single component resin binder system (about 17-18%), wetting agents (about 2%), lubricant (1%) and low density carbon black (3%). Two 1 gallon jar mills were prepared for each variation which contained about one third volume of 5/8 inch steel balls per jar. Also, each mill was formulated to produce 2800 grams of non-volatile coating product for 1800-2600 coated linear feet (6 inch width). At least 1500 feet was required for signal tests (write current/output). Magnetic characterization was performed throughout the milling process on small draw down samples using the LDJ model 7500A B-H meter at 60HzAC. Measurements were recorded about every two hours through the final letdown prior to coating. Coating was achieved at a thickness of 240-280 microinches. The rolls were then slit and submitted for signals testing.

Initial results indicated an unusual variation in the coercivity and orientation ratio. Subsequently, a quick test was performed by milling a small slurry of α-Fe_2O_3, resin and solvent with incrementally increasing amounts of γ-Fe_2O_3 on a paint shaker. Magnetic measurements were made after each addition using the B-H meter on small draw down samples.

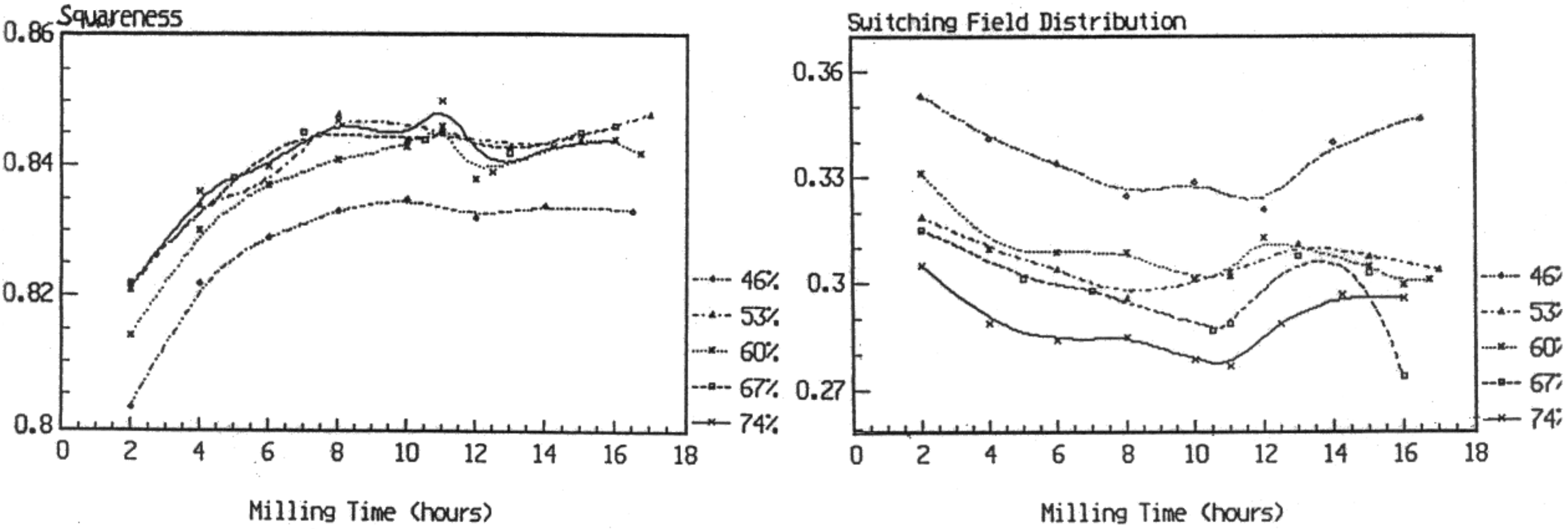
Results & Discussion

Magnetic properties were tabulated for each of the five variations at 2-3 hour intervals throughout the milling process. From the data, plots of each magnetic property against milling time were generated and are shown in Figure 2.



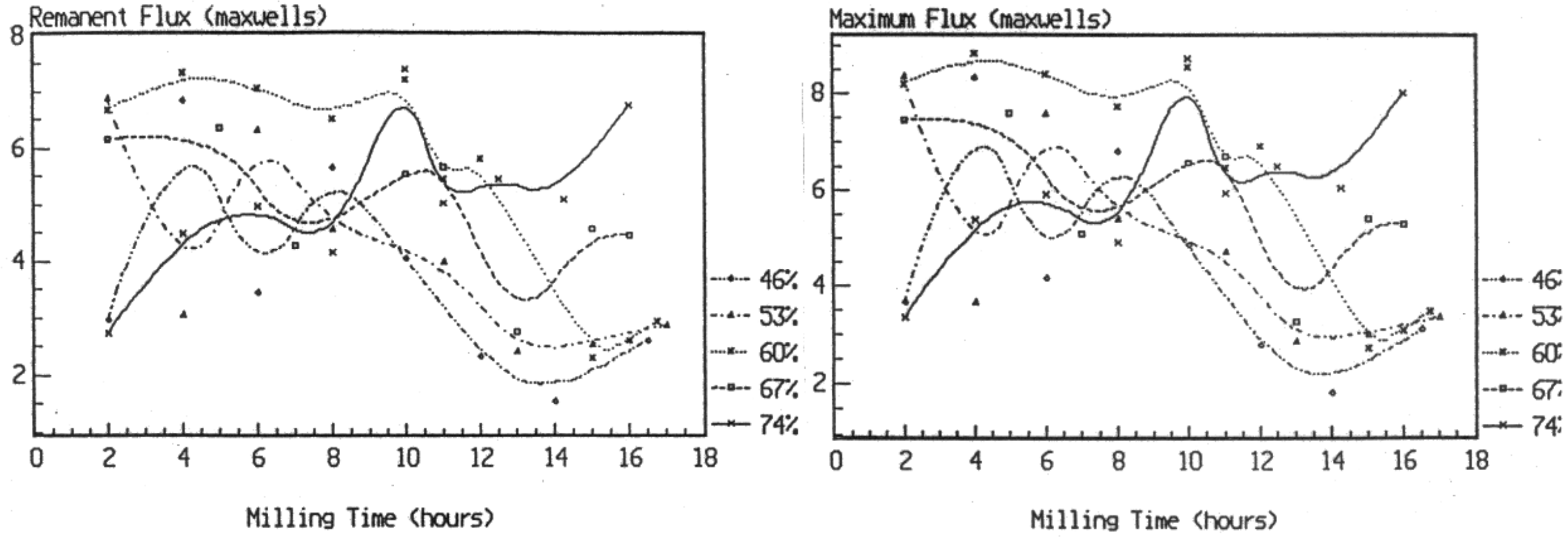
a) Coercivity vs. Milling time

(b) Orientation vs. Milling time



(c) Squareness vs. Milling time

(d) Switching Field vs. Milling time



(e) Remanent flux vs Milling time

(f) Maximum flux vs. Milling time

Figure 2. Magnetic Properties vs. milling time for the five oxide variations.

As seen in Figure 2, the measured coercivity at any particular time decreases as the concentration of γ-Fe_2O_3 increases. The squareness increases and the switching field distribution is reduced as the gamma oxide content increases. It is not certain what effect the α-Fe_2O_3 concentration has on orientation or maximum and remanent flux. However, all four properties appear to vary along open curves for any given oxide concentration throughout the milling process except the coercivity which varies similarly only after the beginning of the second phase of milling (10 - 11 hours).

A graph of the initial coercivity values (after 2 hours milling) at each oxide level is given in Figure 3 which indicates a linear variation in coercivity with γ-Fe_2O_3 concentration over the range of 46 - 74%.

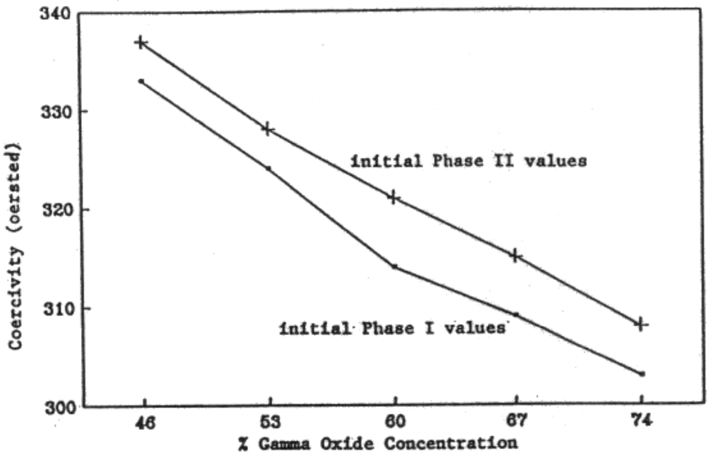


Figure 3. Initial coercivity vs γ-Fe_2O_3 concentration.

Let us follow the trends in Figures 2 & 3 and assume that all four properties, the coercivity H_c, orientation OR, squareness SQ and switching field distribution SFD, vary parabolically over milling time and linearly with γ-Fe_2O_3 concentration as represented by

$$P = c + bt + at^2 \tag{1}$$

where P is a magnetic property, t is the milling time in hours, c, b and a are coefficients whose values depend linearly upon the % concentration of γ-Fe_2O_3. A quadratic was chosen for simplicity; actual functional forms may follow bell curves, hyperbolas or higher order polynomials.

Computer curve fits were generated using Eq. (1) for each property at each oxide level (correlation R^2 values were generally 90 - 99%). Also, linear relationships were produced for c, b and a in terms of the % γ-Fe_2O_3 concentration, x, and are tabulated in Table 1.

Table 1. Values for the three coefficients in Eq. (1).

H_c	for x > 10 hrs.	c = -3.35786x + 388.971	b = 0.30079x + 1.44586	a = -0.00964x - 0.11946
OR	for all x	c = -0.01949x + 3.15870	b = 0.00325x - 0.06741	a = -0.00017x + 0.00426
SQ	for all x	c = 0.00229x + 0.644044	b = -0.00004x + 0.00901	a = 0.000001x - 0.00035
SFD	for all x	c = -0.00191x + 0.45827	b = 0.00005x - 0.01162	a = -0.000002x + 0.00058

Note: orientation ratio is considered a decreasing function as Fig.2(b) reflects but a later test indicates the contrary as expected .

The optimum degree of particle deagglomeration is achieved when milling is stopped at the point where H_c, OR and SQ are maximized and SFD is at a minimum. These points correspond to the peaks of the functional parabolic models representing each property. Thus the optimum milling time, t_{peak} is found by setting the derivative of Eq.(1) to zero,

$$t_{peak} = \frac{-b}{2a}$$

where either a or b is negative. Peak milling times for H_c, OR, SQ and SFD for the five oxide variations are plotted in Figure 4.

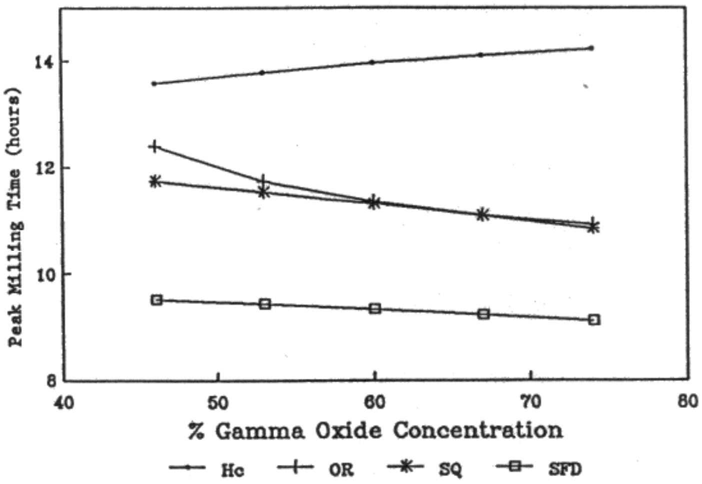


Figure 4. Peak (optimum) milling time vs γ-Fe_2O_3 concentration for H_c, OR, SQ and SFD.

As revealed in Figure 4, t_{peak} varies about an hour between Hc and SFD, and about half an hour for each individual property over the range of 46 - 74% γ-Fe_2O_3 concentration.

Magnetic characterization of the milling/dispersion process for a given oxide concentration is well illustrated by examining an overlay of all four properties. A plot of the $c + bt + at^2$ model functions for H_c, OR, SQ and SFD is shown in Figure 5 for $x = 65.5\%$.

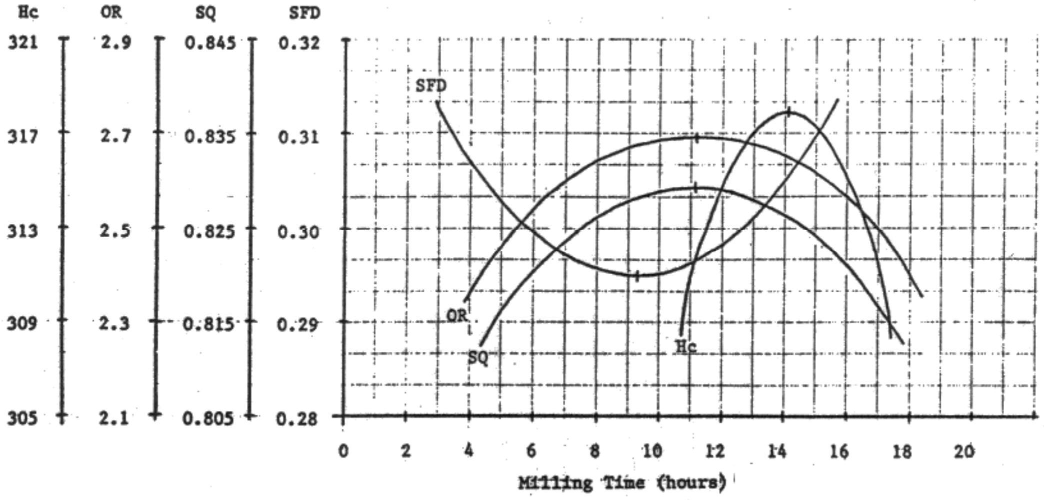
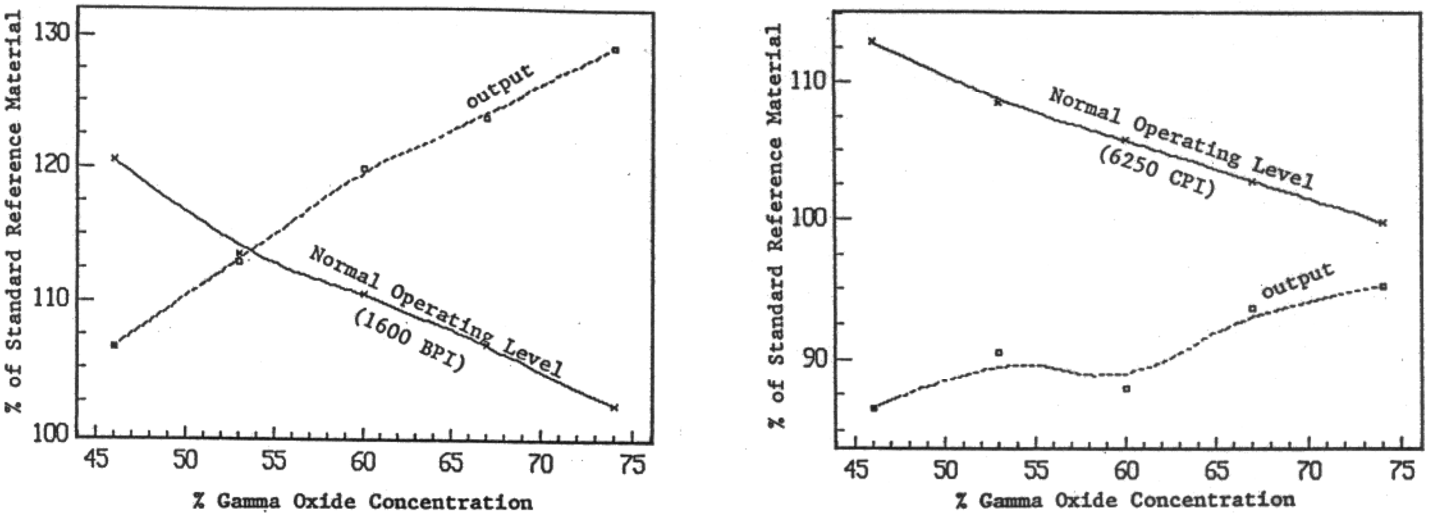


Figure 5. Scaled model representations of H_c, OR, SQ and SFD over milling/dispersion time.

Ideally, t_{peak} for all four properties should coincide. The peak time difference between Hc and SFD is 4.8 hours for x = 65.5% and about 4 hours when x = 46%. The condition where all four peak times coincide is not possible and is unrealistic. The fact that t_{peak} for H_c occurs in the second phase of milling (starting at about 10 hours) is considered to be unique to GMI technology.

The normal operating level (write current) and output (amplitude) based on ANSI standards were determined for each oxide variation. Representative graphs are shown in Figure 6 for two standard recording densities (1600 BPI and 6250 CPI).



(a) Signal response at moderate (1600 BPI) recording density.

(b) Signal response at high (6250 CPI) recording density.

Figure 6. Write current and output for the five variations.

ANSI specifications require that output levels for 1600 BPI be within 90 - 125% of the standard reference and 60 - 140% for 6250 CPI. The normal operating level is proportional to the tape coercivity (compare to Figure 3). The output is proportional to the γ-Fe_2O_3 concentration.

Finally, as discussed in the experimental section, a quick test was performed where small increments of γ-Fe_2O_3 were added to a simple α-Fe_2O_3 slurry to explore possible interaction effects between the two Fe_2O_3 forms. The results are tabulated in Table 2.

Table 2. Magnetic properties for a small α-Fe_2O_3 test slurry with incremental additions of γ-Fe_2O_3. Milling time was 6 - 8 hours. Each draw down sample was tested 3 times and averaged. Test repeatability is indicated by the % deviation (std.dev./average X 100) for each individual sample. Applied field was 1000 oersteds.

%-γ-	Coercivity		Remanent Flux		Maximum Flux		Orientation		Squareness		Switching Field	
oxide	avg	% dev	avg	% dev	avg	% dev	avg	% dev	avg	% dev	avg	% dev
2	389	0.86	0.130	2.56	0.189	3.88	2.70	9.26	0.688	2.33	41.50	133
5	391	0.68	0.247	2.16	0.340	1.67	2.74	0.36	0.727	2.52	35.19	131
10	392	0.26	0.386	1.12	0.508	0.67	2.96	1.80	0.759	1.80	38.19	129
16	388	0.17	0.998	0.30	1.270	0	2.86	0	0.789	0.34	1.54	43.6
20	394	0.09	1.110	0	1.400	0.24	2.91	2.40	0.793	0.25	1.52	25.5
26	376	0.27	1.850	0.18	2.300	0.14	3.02	0.55	0.805	0.29	1.26	11.8
31	372	0.09	2.320	0.14	2.830	0.59	3.04	1.54	0.813	0.04	0.466	1.22
36	368	0.18	2.900	0.12	3.420	0.29	3.19	0.84	0.820	0.41	0.451	1.03

Graphs of some of the data in Table 2 are given in Figure 7.

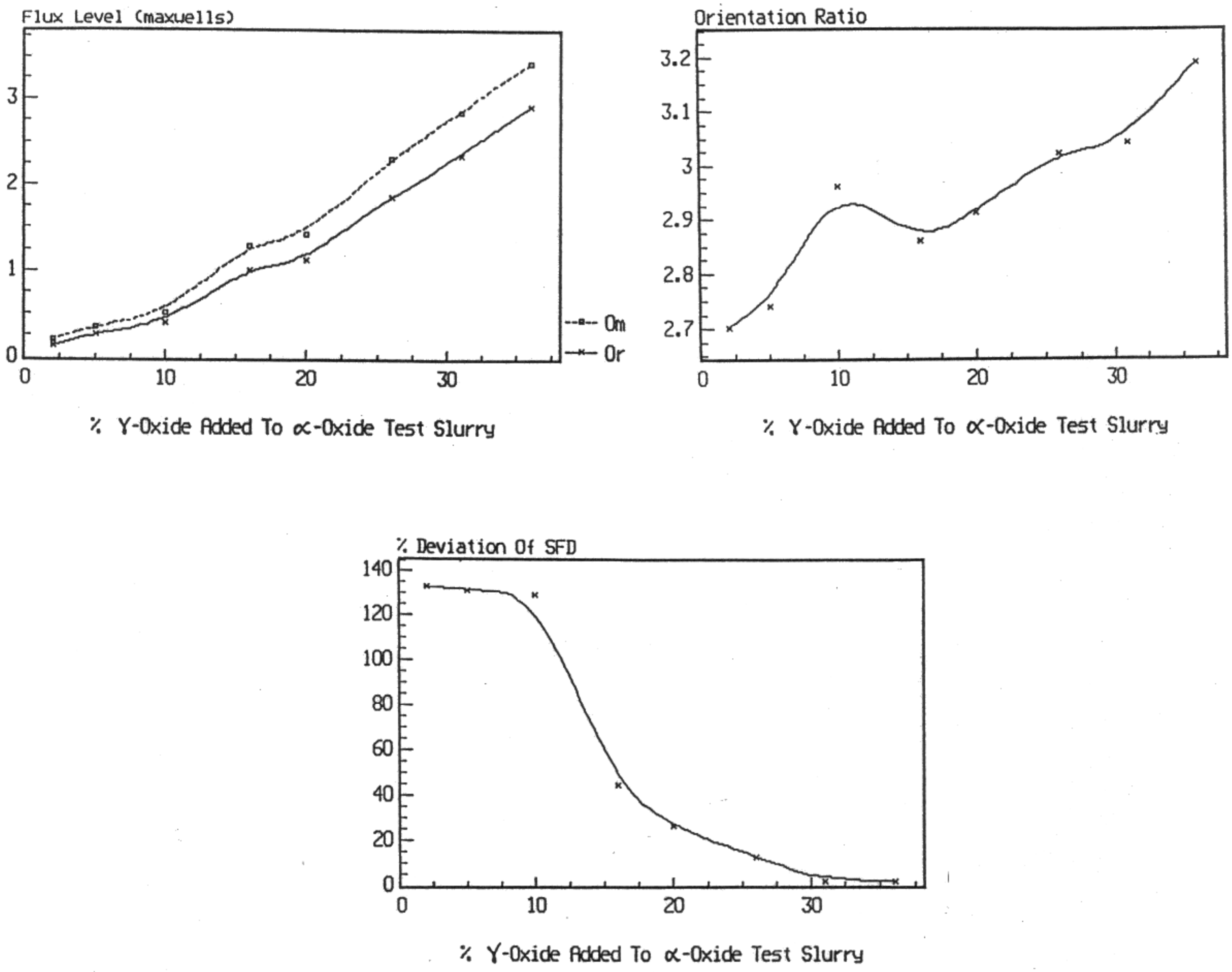
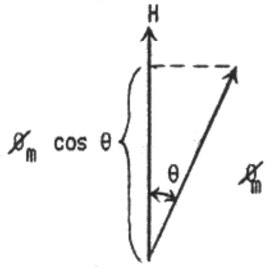


Figure 7. Plots of remanent and maximum flux, OR and SFD deviation vs. increasing γ-Fe_2O_3 portion for a small sample.

As expected, OR increases, flux levels increase (linearly) and the variation in SFD is reduced as the γ-Fe_2O_3 portion increases.

Based on all information gathered in this study, the following statements can now be made. As the concentration of γ-Fe_2O_3 (magnetic oxide) is increased, particle orientation improves (reflected by increases in both the squareness and orientation ratio), the variation in particle coercivities improves (SFD decreases) and the coercivity slightly decreases.

Before concluding the discussion section, a brief description of the four magnetic properties is in order. Longitudinal squareness SQ is the ratio of the component of remanent flux $\varnothing_r$ aligned parallel with the field H to the maximum remanent flux $\varnothing_m$ attainable at perfect alignment. As illustrated below, SQ can be thought of as the cosine of the average angle $(\cos \theta)_{ave}$ between $\varnothing_m$ and H. This angle is an important parameter in the description of dipole moments and induction energy in magnetic materials. Squareness is an indication of particle orientation. The orientation ratio OR is the ratio of remanent flux in the longitudinal (machine) direction to that in transverse transverse (perpendicular) direction. It is a numerical measure of how much greater particle alignment in the machine direction is than alignment in the transverse direction. Both OR and SQ are a reflection of the particle shape anisotropy. Switching field distribution SFD is a measure of the variation in particle coercivities throughout the sample as measured by the half peak width of the differentiated B-H loop. Wide SFD numbers mean a large distribution in particle size, shape and interactions. SFD values produced from the B-H meter are equal to the fractional variation in coercivity; multiplication of the SFD value by the recorded coercivity gives the actual (average) H_c range in oersteds. Also, multiplication of SFD by 100 gives the percent variation in coercivity. The coercivity H_c of a magnetic particle is a measure of its strength as a magnet. For a coating, the measured H_c is an average of all the magnetic particles in the coating. The exact roles of anisotropy, spontaneous magnetization and exchange interaction effects will be discussed in future reports.



$$SQ = \frac{\varnothing_r}{\varnothing_m}$$

$$SQ = \frac{\varnothing_m (\cos \theta)_{ave}}{\varnothing_m}$$

$$SQ = (\cos \theta)_{ave}$$

EPOCH FORMULATION WORKSHEET

HH0311 50% PKHH 50% 5701

NV BATCH SIZE (GRAMS): 3000.0
PHASE I SOLIDS (%): 46.0
PHASE II SOLIDS (%): 32.5
PHASE III SOLIDS (%): 32.0
RESIN A SOLIDS (%): 14.0
RESIN B SOLIDS (%): 14.0

SOLVENT A (%): 100.0
SOLVENT B (%): 0.0
SOLVENT C (%): 0.0
MILL: JM-025 DATE:
COATING:

COMPONENT	NV WT., %	COMPONENT NV, %	NV LOAD, grams	TOTAL LOAD, grams	BATCH LOAD, grams
		PHASE I		batch factor =	0.50
GAMMA-FERRIC OXIDE	65.50	100.0	1965.0	1965.0	982.5
ALPHA-FERRIC OXIDE	6.50	100.0	195.0	195.0	97.5
WETTING AGENT A	0.90	100.0	27.0	27.0	13.5
WETTING AGENT B	0.90	100.0	27.0	27.0	13.5
RESIN A	7.20	14.0	216.0	1542.9	771.4
SOLVENT A				1525.8	762.9
SOLVENT B				0.0	0.0
SOLVENT C				0.0	0.0
	81.00	46.0	2430.0	5282.6	2641.3
		PHASE II			
RESIN A	1.80	14.0	54.0	385.7	
RESIN B	9.00	14.0	270.0	1928.6	964.3
CARBON	4.00	100.0	120.0	120.0	60.0
WETTING AGENT A	0.30	100.0	9.0	9.0	4.5
FUNGICIDE	0.10	100.0	3.0	3.0	1.5
CATALYST	0.30	100.0	9.0	9.0	4.5
LUBRICANT A	1.00	100.0	30.0	30.0	15.0
SOLVENT A				1232.1	616.1
SOLVENT B				0.0	0.0
SOLVENT C				0.0	0.0
	97.50	32.5	2925.00	9000.0	4307.1
		PHASE III			
CROSSLINKER	2.50	70.0	75.0	107.1	53.6
SOLVENT A				267.9	133.9
SOLVENT B				0.0	0.0
SOLVENT C				0.0	0.0
	100.00	32.0	3000.0	9375.0	4494.6

RESIN PREPARATION SHEET

MILL:	JM–025
BATCH FACTOR:	1.20

COMPONENT	COMPONENT NV, %	NV LOAD, grams	TOTAL LOAD, grams	BATCH LOAD, grams
RESIN A	100.0	270.0	270.0	324.0
SOLVENT A			1658.6	1990.3
SOLVENT B			0.0	0.0
SOLVENT C			0.0	0.0
	14.0	270.0	1928.6	2314.3

COMPONENT	COMPONENT NV, %	NV LOAD, grams	TOTAL LOAD grams	BATCH LOAD, grams
RESIN B	100.0	270.0	270.0	324.0
SOLVENT A			1658.6	1990.3
SOLVENT B			0.0	0.0
SOLVENT C			0.0	0.0
	14.0	270.0	1928.6	2314.3

COMPONENT	MATERIAL	VENDOR
GAMMA–FERRIC OXIDE	HH311	MAGNOX
ALPHA–FERRIC OXIDE	R311	MAGNOX
WETTING AGENT A	CENTROLEX–P	CENTRAL COYA
WETTING AGENT B	GAFAC RE–610	GAF CORPORATION
RESIN A	ESTANE 5701	BF GOODRICH
RESIN B	PKHH	UNION CARBIDE
SOLVENT A	THF	DUPONT
SOLVENT B	MIBK	DELTA
CARBON	XC72R	CABOT
FUNGICIDE	BUSAN 72	BUCKMAN LABS
CATALYST	FE(AA)3	SHEPERD CHEMICAL
LUBRICANT A	BES	VAN WATERS
CROSSLINKER	CB–701	MOBAY
BASEFILM	140OPB	DUPONT