## PATENT SPECIFICATION

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## (54) ACICULAR COBALT-MODIFIED MAGNETIC IRON OXIDE AND ITS MANUFACTURE

(71) We, BASF AKTIENGESELLSCHAFT, a German Joint Stock Company of 6700 Ludwigshafen, Federal Republic of Germany, do hereby declare the invention, for which we pray that a Patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following Statement:—

The present invention relates to acicular, cobalt-modified gamma-iron (III) oxide and to its manufacture.

Accordar gamma-iron (III) oxide has for a long time been employed extensively as a magnetizable material in the manufacture of magnetic recording media. However, as a result of continuing development in recording technology, there is an increasing need for magnetic materials which, above all, have a higher coercive force than gamma-iron (III) oxide. Although it is known that the coercive force of iron oxides can, under certain circumstances, be substantially increased by modification with cobalt, the increase depending on the amount of cobalt added, such modified materials have a number of undesirable properties, in particular the residual induction and coercive force thereof are unstable to thermal and mechanical factors. Materials having such disadvantages are unsuitable for use in magnetic recording media.

Cobalt-modified acicular iron oxides may be obtained by a variety of processes. According to German Patent 1 112 725 and 1 226 997, modification with cobalt is easily achievable by coprecipitation of iron hydroxide and cobalt hydroxide in the manufacture of goethite, since the subsequent conversion of the cobalt-containing goethite to the corresponding gamma-iron (III) oxide may be carried out in the conventional manner. German Laid-Open Application DOS 2 100 390 employs a similar

German Laid-Open Application DOS 2036612 discloses that a cobalt compound can also be preclipitated onto the surface of a gamma-iron (III) oxide. The cobalt is introduced into the oxide lattice by subsequent heating at from 380 to 400°C. German Laid-Open Application DOS 2 243 231 proposes heating at a temperature of only 80—300°C. German Laid-Open Application DOS 2 022 013 discloses a further method of obtaining cobalt-containing acicular iron oxides, in which acicular FeOOH, Fe<sub>2</sub>O<sub>3</sub> or Fe<sub>3</sub>O<sub>4</sub> is mixed with a cobalt-containing liquid, the slurry is dried and the mass is then converted to gamma-iron (III) oxide by conventional methods. In the process of German Published Application DAS 2 221 218, a cobalt-containing goethite or alpha-Fe<sub>2</sub>O<sub>3</sub> is converted in the conventional manner to gamma-iron (III) oxide, but only after it has first been heated at from 600 to 800°C. According to German Published Application DAS 1907236, another method of manufacturing cobalt-containing accular gamma-iron (III) oxide is to suspend gamma-iron (III) oxide, or an oxide obtained as an intermediate in its manufacture, in an aqueous medium, precipitate a cobalt compound onto the oxide, and then heat the material at a temperature sufficiently high to decompose the cobalt compound. Preferably, this is done in an inert gas atmosphere at above 370°C. Such modified iron oxides are then, if necessary, subjected in the conventional manner to reduction and oxidation to obtain the end product. The partial reduction of the cobalt-modified gamma-iron (III) oxides obtained by this process, in order to increase their coercive force, has also been proposed. In addition to these processes, it has also already been proposed, in German Laid-Open Application

DOS 2 308 791, to apply metallic cobalt to magnetite and treat the resulting coated particles in an inert atmosphere at from 100 to 600°C.

	2	1,583,256	2
		Most cobalt-containing acicular iron oxides do not have entirely satisfactory magnetic properties and are thermally and/or mechanically unstable. The desired high coercive force is in most cases only achieved by a relatively high cobalt content which	
_	5	then results in the known disadvantages. Reducing the amount of cobalt and at the same time increasing the treatment temperature does no give products which, when employed in magnetic recording media, conform to the expected requirements.  The present invention seeks to provide a magnetic material, based on iron oxides, which, although having a very low cobalt content, gives a very high coercive force, which the effect of temperature on the coercive force and residual industries in very	5
	10	whilst the effect of temperature on the coercive force and residual induction is very slight, can be manufactured in a simple and economical manner, and, when employed for the manufacture of magnetic recording media, give a high signal-to-print-through ratio and a high ratio of the recorded signal to the residual signal after erasure as well as good thermal and mechanical stability.	10
٠	15	According to the present invention there is provided an acicular cobalt-modified gamma-iron (III) oxide containing divalent iron and having a cobalt content of from 0.5 to 10 percent by weight, based on the cobalt-modified iron (III) oxide, which material contains from 1.2 to 18 percent by weight of divalent iron, based on the cobalt-modified iron oxide, and has a TA value (as hereinafter defined) of less than 2.5.	15
	20	According to the invention there is also provided a process whereby this material is manufactured by applying a cobalt compound to a magnetize produced by reduction of acicular hydrated iron oxide or its dehydration product and oxidizing the resulting coated magnetite in an oxygen-containing atmosphere at from 100 to 200°C until the residual content of divalent iron is from 1.2 to 18 percent by weight, based on the cobalt-modified iron oxide.	20
	25	According to the process of the invention, the cobalt-modified gamma-iron (III) oxide containing from 1.2 to 18 percent by weight of divalent iron and having a TA value of less than 2.5 is manufactured from magnetite. The latter may be manufactured in a conventional manner by reduction of acicular hydrated iron oxide, especially in the form of goethite, or by reduction of the alpha-iron (III) oxide obtained therefrom by	25
	30	dehydration at from 200 to 600°C, the reduction being carried out with a gaseous reducing agent, preferably hydrogen, at from 300 to 400°C. Advantageously, the magnetite thus obtained is suspended in water, a coballt salt solution is added to this suspension and the cobalt hydroxide is precipitated onto the magnetite by adding an alkali, particularly an alkali metal hydroxide. The cobalt salt solution used is, as a rule,	30
	35	an aqueous cobalt sulfate solution from which the cobalt hydroxide is precipitated by means of alkali metal hydroxide solution at a pH above 8. The amount of cobalt compound added is chosen so that the resulting end product from the process of the invention contains from 0.5 to 10 percent by weight of cobalt. After filtering off and	35
	40	drying, the magnetite/cobalt hydroxide mixture is oxidized in the presence of oxygen at from 100 to 200°C, preferably at from 110 to 180°C, until the iron (II) content is from 1.2 to 18 percent by weight, based on the end product. The drying temperature must not exceed the upper limit of the stated oxidation temperature range.  The desired iron (II) content is advantageously obtained by selection of the residence time of the product in the oxidation stage. It has proved advantageous to use	40
,	45	an air/nitrogen mixture in order to ensure that the oxidation takes place uniformly, and to avoid local overheating. In general, it is possible, by means of a few experiments, to determine the rate of oxidation under a given set of conditions, so as to ascertain the residence time. The iron (II) content is simple to determine by analysis, e.g. cerimetrically.	45
	50	The above partial oxidation can be carried out in the same way in the course of drying the filtered-off magnetite/cobalt hydroxide mixture.  In carrying out the process of the invention, it has proved advantageous to provide the magnetite intermediate, e.g. goethite or hydrated iron oxide, with a protective	50
	55	coating which prevents the fine acicular particles from sintering at the high temperature of the reduction reaction. A particularly suitable method of producing a generally inorganic protective coating, which substantially encases the pigment and is in general present in amounts of from 0.1 to 6 percent by weight, especially from 0.5 to 3 percent by weight, based on the treated iron oxide or hydrated iron oxide, on the surface of the acicular pigment, is to treat the pigment with an inorganic compound, e.g. an	55
	60	oxygen acid of phosphorous and/or boron or a salt of such an acid. It is also possible to treat the surface of the pigment with a hydroxide or oxide of alluminum, silicon, titanium, zirconium or chromium, which can of course also be produced on the pigment surface from a hydrolyzable salt of one of these elements, e.g. a solution of an	60
٠	65	aluminum salt, titanium salt or zirconium salt, by adding alkali, or from an alkali metal silicate solution. A particularly suitable method is to add phosphoric acid, a	65

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	soluble ammonium phosphate or an alkali metal phosphate or pyrophosphate to the acicular pigment. Further details of the production of protective coatings may be found, for example, in Belgian Patent 668 986 and in German Laid-Open Application DOS 1 592 214 and DOS 1 803 783.	
5	Equally, it is advantageous, in the conventional manner, to improve the dispersibility and magnetic orientation of the finished gamma-iron (III) oxides for the purpose of the manufacture of magnetic recording media, by treating the magnetic	5
10	intermediate with an organic compound, e.g. an alkyl or cycloalkyl phosponate, phosphite or phosphate, a corresponding amide of a phosphorous-containing acid, a hydrophobic aliphatic carboxylic acid, or a reaction product of an alkaline earth metal compound and an alkylphenol with up to 3 alkyl radicals of 4 to 24 carbon atoms.	10
	The magnetic materials of the invention are distinguished by high coercive force and residual induction, and in particular the low temperature dependence of these properties should be mentioned. Thus, these new materials exhibit values of the tem-	
15	perature dependence, i.e. TA values, of less than 2.5. The TA value is the sum of the quatient of the coercive force at $-100^{\circ}$ C to the coercive force at $+25^{\circ}$ C and of the relative remanence $M_{\rm R}/M_{\rm S}$ at $-100^{\circ}$ C to that at $+25^{\circ}$ C.  The instability to mechanical and thermal stresses which conventional cobalt-	15
20	containing magnetic iron oxides exhibit and which is essentially due to the substantial amount of cobalt present in the crystal lattice in order to achieve high coercive forces is substantially avoided by the particular structure of the magnetic iron oxides of the invention. These properties prove equally advantageous when these materials are employed for the manufacture of magnetic recording media.	20
25	In particular, the improvement in the signal-to-print-through ratios achieved with the products according to the invention was surprising. It was known that magnetic recording media using either magnetite or cobalt-modified gamma-iron (III) oxide were	25
30	unsatisfactory because of their increased crosstalk. If, however, the material manufactured according to the process of the invention is used for the manufacture of magnetic recording media, there is a substantial increase in the signal-to-print-through ratio in addition to the other improvements.  As a result of the special products of the invention retaining a high proportion of shape anisotropy, the magnetic recording media also show a surprisingly high orientation ratio, i.e. a high ratio of residual induction in the playing direction to that	30
35	in the crosswise direction.  To produce magnetic coatings, the gamma-iron (III) oxide manufactured according to the invention is dispersed in polymeric binders. Suitable binders for this purpose are conventional compounds, e.g. homopolymers and copolymers of vinyl derivatives, polyurethanes, polyesters and the like. The binders are used in the form of solutions in	35
40	suitable organic solvents which may contain further additives, e.g. to increase the conductivity and abrasion resistance of the magnetic coatings. On milling the magnetic pigment, the binder and any additives, a homogeneous dispersion is obtained, which is applied to rigid or flexible bases, e.g. films, discs or cards, by conventional methods. Immediately after applying the dispersion to the base, the magnetic particles are	40
45	orientated, in the desired recording direction, by means of a magnetic field. Only then are the magnetic coatingse dried and, if desired, subjected to a surface treatment.  The Examples which follow illustrate the invention. They relate to figures which show the dependence of the coercive force and relative remanence on the temperature.	45
50	The magnetic properties, i.e. the coercive force $H_c[kA/m]$ , the specific remanence $M_B/\rho$ [nTm <sup>3</sup> /g] and specific saturation magnetization $M_S/\rho$ [nTm <sup>3</sup> /g], were measured in a vibrating sample magnetometer at a field strength of 160 kA/m. The	50
	magnetic orientability of the particles was determined by means of a preliminary test and quoted as the RF <sub>B</sub> .  For this latter test, about 1 g of the magnetic powder is introduced into a two-	
55	component epoxy resin, so that the proportion by volume of the magnetic powder is about 10%. The powder is thoroughly mixed with the two-component resin between counter-rotating glass discs and is then spread in a thin layer and cured at 70°C in a homogeneous magnetic field of 800 kA/m. This results in different degrees of orientation of the magnetic particles parallel to the magnetic field, the degree depending	55
60	on their process of manufacture. This orientation is measured in terms of the orientation ratio, RF <sub>E</sub> , the quotient of the residual induction along, and crosswise to, the direction of orientation.  To measure the temperature dependence of the coercive force and the relative	60
65	remanence and to determine the TA value, the powder samples were examined in a field of 800 kA/m at from $-100$ to $+140$ °C, in each case carrying out a heating and cooling cycle.	65

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5	The suitability of the materials for use in the manufacture of magnetic recording media was determined by testing identically manufactured magnetic recording media, produced by dispersing the magnetic pigments obtained in a solution of a copolymer of vinyl chloride, dimethyl maleate and diethyl maleate and a thermoplastic polyester-urethane using conventional dispersing aids, applying this dispersion by the conventional method to a 12µm thick polyethylene terephthalate film in such a thickness that, after drying, a 5 µm thick magnetic coating remains, orienting the coating, whilst still liquid, by means of a magnetic field, and drying it. The residual induction $M_R$ and saturation magnetization $M_S$ [mT] of the tape samples were measured in a field of 160 kA/m, the magnetic orientation ratio RF was obtained from the ratio of the residual induction in the longitudinal direction to that in the crosswise direction and the signal-to-print-through ratio $K_o$ was measured in accordance with DIN 45,519.	5
	EXAMPLE 1.	
15	Using the process described in German Published Application DAS 1 204 644, a goethite having a mean particle length of 0.69 $\mu$ m, an average length to thickness ratio of 20.4 and a specific surface area of 29.6 m <sup>2</sup> /g is manufactured in alkaline medium. After dehydration, the resulting goethite is reduced to magnetite in a stream	15
20	of hydrogen at 380°C.  400 parts of this magnetite are suspended in 8,000 parts of water by means of a high-efficiency stirrer. An aqueous solution of 48 parts of CoCl <sub>2</sub> . 6 H <sub>2</sub> O are added to this suspension and the pH is brought to 11.2 with 2-normal sodium hydroxide solution. After stirring thoroughly for a further half hour, the solid, consisting of magnetite	20
25	and cobalt hydroxide, is filtered off and washed with water until the filtrate has a pH of 7. The filter cake is then dried for 72 hours at 60°C under a pressure of 100 mm Hg.  Three similarly prepared samples A, B and C are partially oxidized in a stream of nitrogen and air (in the ratio of 4:1) with constant agitation, under the conditions	25
30	shown in Table 1.  The measurements obtained are shown in Table 1 and the temperature dependence of the coercive force $H_c$ and of the relative remanence $M_R/M_S$ is shown in Figures 1 to 3.	30
35	COMPARATIVE EXPERIMENT 1.  A sample D consisting of magnetite onto which cobalt hydroxide has been precipitated is prepared as described for samples A—C in Example 1, and is oxidized as described in Example 1 and at a temperature of 250°C as recorded in Table 1. The measurements obtained are also shown in Table 1. The temperature dependence of	35

measurements obtained are also shown in Table 1. The temperature dependence the coercive force  $H_c$  and of the relative remanence  $M_B/M_S$  is shown in Figure 4.

	TA value			2.3	2.4	2.3		3.9	<u>.</u>				
	स्य च			3.0	3.0	2.8		2.1				٠.	
TABLE 1	R H	(% = 1.2 mg mn <sup>3</sup>		41.0	40.8	6.04		41.6			frace ettite, mple 5	man nder le 2,	ence 10
	$^{\rm M}_{ m R}/^{ m M}_{ m S}$			0.54	0.54	0.54		0.58			g a specific suerted to magnontrast to Exam	pressure of 50 n takes place u shown in Tabi	relative reman nple C).
	ह्ये ही			43	43	43		84			3 µm is convicample 1. In conv	artial oxidation	orce He and B) and 7 (san
	MS/8 nTm <sup>2</sup>	ю		42	79	42		83	-	EXAMPLE 2.	d in Example length of 0.6 stribed in Ex	subsequent p	ne coercive for section of the secti
	Fe <sup>2+</sup> content	[%]		3.6	3.6	3.2		3.4		EXA	nred as describe mean particle dydroxide, as des	Example 1, the Table 2. The	ependence of the
	Oxidation ra- Duration	[mim]		120	98	75		58	<b>-</b>	A goethite manufactured as described in Example 1 and having a specific surface area of 36.8 m²/g and a mean particle length of 0.63 µm is converted to magnetite, and treated with cobalt hydroxide, as described in Example 1. In contrast to Example	A goethite manufactured as described in Example 1 and having a specific sunface area of 36.8 m²/g and a mean particle length of 0.63 µm is converted to magnetite, and treated with cobalt hydroxide, as described in Example 1. In contrast to Example 1 the magnetic contrast to a contrast to example 1.	Hg. As a modification of Example 1, the subsequent partial oxidation takes place under the conditions shown in Table 2. The values measured are also shown in Table 2,	whilst the temperature dependence of the coercive force H <sub>c</sub> and relative remanence $M_R/M_S$ is shown in Figure 5 (sample A), 6 (sample B) and 7 (sample C).
	O Tempera	Oxi Tempera- ture [°c]		150	1.65	1.80		250			ares 5 and	Hg.	whi 10 M <sub>E/</sub>
			Example 1	Sample A	Sample B	Sample C	. Comparative Experiment 1	Sample D					

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	Oxidation Tempera- Dura ture [°C]	tion in]	Fe <sup>2+</sup> $M_S/S$ $M_R/S$	MS/8	MR/8	$^{\rm R/M_S}$	$H_{c}$ $\begin{bmatrix} \frac{kA}{m} \\ 0 \end{bmatrix}$ $(S = 1.2 \frac{mg}{mm^{3}})$	TA value
Example 2 Sample A Sample B Sample C	130	300	2.65	78	43	0.55	47.9	2.4
	150	105	2.80	79	44	0.56	47.6	2.8
	220	31.5	3.22	76	43	0.57	46.3	2.8

S EXAMPLE 3.

A magnetite with cobalt precipitated onto it, manufactured as described in Example 2, is partially oxidized in a stream of air and nitrogen, in the ratio of 1:4, at 150°C for up to 105 minutes. During the oxidation phase, samples are taken. The values measured on these samples are summarized in Table 3. 2

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			T.	ABLE 3		
		Fe <sup>2+</sup> content [%]	M <sub>S</sub> /3 \[\frac{nTm^3}{g}\]	$\begin{bmatrix} \frac{M_R}{s} \end{bmatrix}$	M <sub>R</sub> /M <sub>S</sub>	$(9 = 1.2 \frac{\text{mg}}{\text{mm}^3})$
Example	e 3					
Sample	вı	17.6	87	48	0.55	42.9
11	в 2	13.3	85	. 47	0.55	45.5
tt .	в 3	10.5	85	47	0.55	45.8
#	в 4	9.0	84	46	0.55	45.7
**	В 5	7.0	83	46	0.55	46.0
11	в 6	4.2	79	44	0.56	46.7
81	в 7	3.0	77	43	0.56	46.7
Ħ	В	2.8	79	- 44	0.56	47.6

## EXAMPLE 4.

A magnetite containing cobalt hydroxide and manufactured as described in Example 1 is partially oxidized for 2 hours at 150°C in a stream of nitrogen and air in the ratio of 4:1. During this oxidation, samples are taken and magnetic tapes are produced from this magnetic material. The content of Fe<sup>2+</sup> in the magnetic pigment and the magnetic properties of the magnetic coating, as well as the data relating to the signal-to-print-through ratio are shown in Table 4.

COMPARATIVE EXPERIMENT 2.

A part of the sample produced for Example 4 is oxidized at 250°C instead of at 150°C.

	24		3	TABLE 4	E C	2 0 7 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0		<b>b</b>
	Fercontent	Σ Ω	≽: દેવ:	MR/MS	FF.	Coating thickness	ness	× °
	[%]	[mT]	[m]			[mn]		[dB]
Example 4				·				
Sample A l	17.4	506	165	08.0	2.2	9.4		-0.5
" A 2	9.5	194	151	0.81	2.1	5.0		-0.5
" A 3	5.7	191	153	08.0	2.0	8.4		+1.0
Comparative Experiment 2	3.4	172	140	0.81	1.6	L·7		-3.0
	A gC	oethite manul	Eifactuared by the	EXAMPLE 5. he process described and susmembed in	ed in German	EXAMPLE 5.  A goethite manufactured by the process described in German Published Application DAS 1.704 6404 is finely millied and suscended in a 20-folid amount of water. The		
S	percent b	is suspension by weight of s	is brought to soybean fecithin iion. Affer vison	7.5 by adding a based on the an	ilittle dilute in nount of goot!	performance of this suspension is brought to 7.5 by adding a little dilute sulfuric acid and 3 percent by weight of soybean lecitlin, based on the amount of goothite, are then introduced into the suspension. After visonous starting for two hours, the mixture is filtered	\$	
	and the treated	reated goethi	goethite is dried in air at 120°C.	ir at 120°C.	on the 400	to meantar a mi Do		
10	hydrogen and mi a stream of nitro	and nitroger of nitrogen.	in the ratio of	of 1:2. The result roxide is precipit.	tring magnetit	hydrogen and nitrogen in the ratio of 1:2. The resulting magnetite is then cooled in a stream of nitrogen. The cobalt hydroxide is precipitated onto the material by adding	. 01	
	a coballt the amou	chloride solutint of cobalt	tion to the mag chiloride employ	gnetlite, suspender red being such as	d in a 10-folk to provide 2	a cobalit chloride solution to the magnetite, suspended in a 10-fold amount of water, the amount of cobalt chloride employed being such as to provide 2 percent by weight		
15	ot cobalit, based deagglomerated precipitated by	, based on the crated by vi- ed by dropw	igorous stirring	agnetite. The ma for one hour. dilute sodium i	gnetite partic The cobalit hydroxide solv	on the amount of magnetite. The magnetite particles are substantially by vigorous stirring for one hour. The cobalt hydroxide is then dropwise addition of dilute sodium hydroxide solution until the pH	15	
	is 8.0. Ti The resul	he entire pre- Iting product	cipitate is filter (I) is partially	ed off, washed n oxidized. The re	reutral and dr sidual conten	is 8.0. The entire precipitate is filtered off, washed neutral and dried in air at 80°C. The resulting product (I) is partially oxidized. The residual content of Fe <sub>3</sub> O <sub>4</sub> and the		
20	magnetic The	properties an product (I)	is then partialli	magnetic properties are shown in Table 5.  The product (I) is then partially oxidized in a rotary tubular furna	rottary tubular	magnetic properties are shown in Table 5.  The product (I) is then partially oxidized in a rotary tubular furnace at 110°C.	20	
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A renewed oxidation stage in the rotary tubular furnace gives product III, and a further pass gives product IV. The results of measurements on these products are summarized in Table 5.

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		Fe <sub>3</sub> 0 <sub>4</sub> content [%]	$\begin{bmatrix} \frac{M_{S}}{S} \end{bmatrix}$	$ \frac{M_{R}/9}{\left[\frac{nTm^{3}}{g}\right]} $	$\frac{H_{\mathbf{C}}}{\left[\frac{\mathbf{k}\Lambda}{\mathbf{m}}\right]}$
Example	5				
Product	I	56	82.7	43.9	43.8
li	II	35	82.5	42.7	45.5
1f	III	20.6	80.3	42.4	46.3
11	IV	14.0	79.6	41.3	46.7
5	WHAT	WE CLAIM IS	S:—		

1. Acicular cobalt-modified gamma-iron (III) oxide which contains divalent iron and has a cobalt content of from 0.5 to 10 percent by weight, based on the cobaltmodified iron (III) oxide, in which the content of divalent iron is from 1.2 to 18 percent by weight based on the cobalt-modified iron oxide, and the product has a TA value (as hereinbefore defined) of less than 2.5.

2. A process for the manufacture of an acicular cobalt-modified gamma-iron (III) oxide as defined in claim 1, in which process a cobalt compound is applied to magnetite produced by reduction of acicular hydrated iron oxide or its dehydration product and the resulting coated magnetite is oxidized in an oxygen-containing atmosphere at from 100 to 200°C until the residual content of divalent iron is from 1.2 to 18 percent by weight, based on the cobalt-modified iron oxide.

3. A process as claimed in claim 2, in which the oxidation is carried out at from 110 to 180°C.

4. A process as claimed in claim 2 or claim 3 and comprising the steps of: —

(1) dissolving a cobalt compound in water,

mixing the resulting solution with acicular magnetite with rapid stirring to provide a homogeneous slurry,

adding an alkali metal hydroxide to precipitate cobalt hydroxide,

separating the solid matter of the resulting slurry and washing and drying it, and

(5) oxidizing the dried residue in air at a temperature of from 110 to 180°C. 5. A process as claimed in claim 2 carried out substantially as described in any

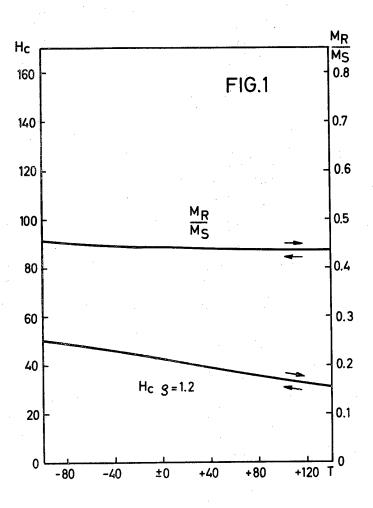
one of the foregoing specific Examples 1, 2, 3, 4 and 5.

6. An acioular cobalt-modified gamma-iron (III) oxide whenever obtained by a process as claimed in any one of claims 2 to 5.

7. A magnetic recording medium manufactured using an acicular gamma-iron (III) oxide, containing cobalt and iron (II), as claimed in claim 1 or claim 6.

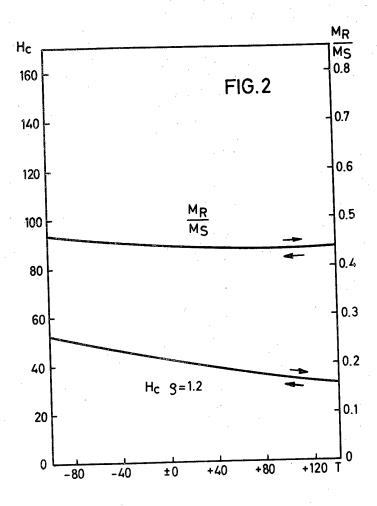
> J. Y. & G. W. JOHNSON, Furnival House, 14—18 High Holborn, London, WOIV 6DE, Chartered Patent Agents, Agents for the Applicants.

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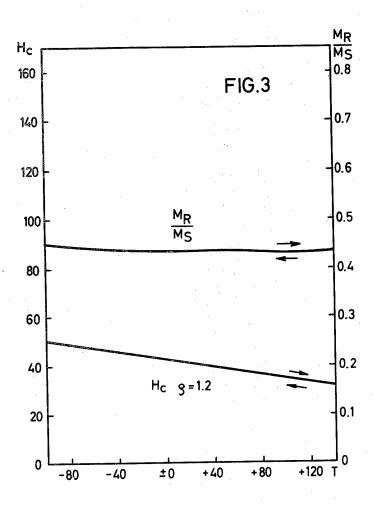
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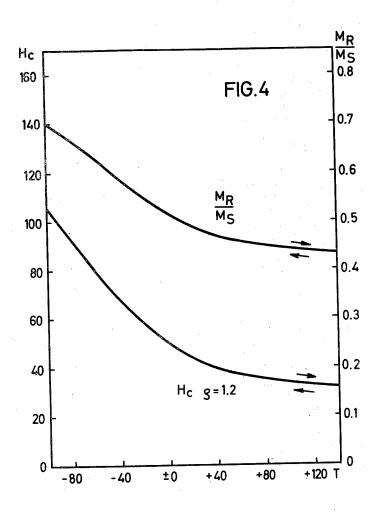
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Sheet 3

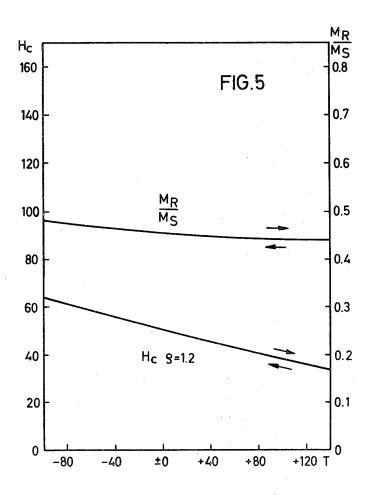


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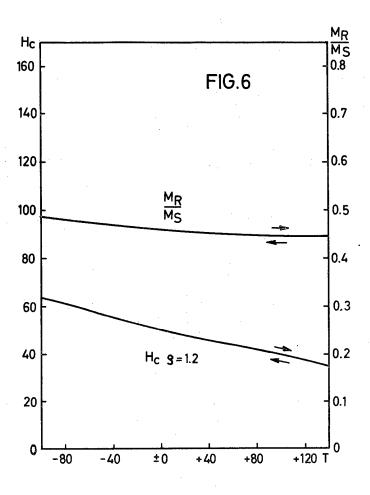
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