Evaluation of Polyurethane Having SO₃Na Group as Magnetic Binder

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ABSTRACT: Magnetic layers were formed by use of polyurethane having SO₃Na group as binder of magnetic particles. A packing degree and surface roughness of magnetic layer were investigated. When magnetic layers were soaked into silicone oil, the silicone oil could penetrate into every void perfectly. The void volume fraction could be estimated by measurement of the weight increase of magnetic layer by soak into silicone oil. Continuous void was formed along with the network structure of magnetic particles. The void in magnetic layer was still continuous after calender treatment. The void fraction of magnetic layer was affected by the intensity of interaction between binder polymer and magnetic particles, and time of formation of flocculation during dry of magnetic paint. Time of the formation of flocculation depended on the steric stabilization by adsorbed polymer, and determined surface roughness of magnetic layer. The increase of SO₃Na content was effective to intensify the interaction between binder polymer and magnetic particles, but it furthered the formation of flocculation structure if solvent of magnetic paint was not suitable for binder polymer.

KEY WORDS Magnetic Tape / Binder / Polyurethane / SO₃Na Group / Void Fraction / Surface Roughness / Continuous Void / Silicone Oil / Flocculation /

Magnetic tapes are generally produced by application of magnetic paints on to a base film usually composed of poly(ethylene terephthalate) (PET) films. Magnetic paints comprise magnetic particles, binder polymers and solvents. Magnetic particles are packed in the magnetic layer over the critical pigment volume concentration (CPVC)¹ for the noise reduction and the improvement of recording density. The properties of layer containing pigment change greatly at CPVC.² This is due to an increase of void volume at CPVC. Minute magnetic particles with high coercive force are suitable for high recording density.³ But such particles are hard to disperse and easy to flocculate. As a result, magnetic layers with such articles have much void and rough surface. The void volume in magnetic layer is usually over 30 vol%.⁴ Good dispersion, high packing and high orientation of magnetic particles in magnetic layer are necessary for high magnetic recording density.⁵ Surface roughness of magnetic layer affects the output of magnetic tape.⁶ Kanai and Amari⁷ represented the relationship between a packing degree of magnetic particles and surface roughness.

The interaction between magnetic particles and binder polymer influences the quality of magnetic dispersion. The use of polymer with hydrophilic groups as magnetic binder is effective to intensify the interaction between magnetic particles and binder polymer.⁸ Mizumura *et al.*⁹ showed that polyesters or polyurethanes having alkaline metal sulfonate groups had an excellent dispersibility to magnetic particles.

Mizuhara *et al.*¹⁰ studied the adsorption of polyvinyl acetate from solution onto glass powders. They pointed out that the extent of adsorption depended strongly upon the sort of solvents in a manner which could be discussed with solubility parameter and size of the polymer coil in the solution. A packing degree of magnetic particles in magnetic layer was influenced by the sort of solvents of magnetic paint.¹¹

Sumiya *et al.*¹² proposed the calculation method of the void volume fraction (f_v) in magnetic layer based on the saturated magnetization and the volume of the magnetic layer. However, in this method the magnetic layer with uniform thickness must be formed and the thickness of the magnetic layer must be measured exactly.

We synthesized various polyurethanes from polyesters containing SO₃Na groups and 4,4'-diphenylmethane diisocyanate. By use of such functional polyurethanes, magnetic paints with good dispersibility can be prepared without high performance dispersion machines such as sand-mills and continuous kneaders.¹³

In this paper, we would like to propose a simple measuring method of f_v and to discuss the properties and the formation process of the void in magnetic layer. Furthermore, influences of SO₃Na content and solvents of magnetic paints on f_v and surface roughness would be discussed according to this void-formation process.

EXPERIMENTAL

Materials

Preparation of Polyurethanes. A typical procedure is as follows. Polyester (A-1) (100 g) was dissolved in 100 g of toluene in the reactor equipped with a thermometer, an agitator, a reflux condenser, and a distilling tube, followed by distilling 20 g of toluene in order to remove water from the solution as the toluene azeotrope. After the reaction mixture was cooled to 60°C, 80 g of 2-butanone (MEK), 7 g of 2,2-dimethyl-1,3-propanediol, 26.5 g of 4,4'-diphenylmethane diisocyanate, and 0.03 g of di-*n*-butyltin dilaurate were added into the A-1 toluene solution. The mixture was stirred at 80°C for 8 h. Then, the concentration of polyurethane prepared was adjusted to 30 wt% by addition of 75.8 g of toluene and 75.8 g of MEK. Polyesters used in this paper were summarized in Table I. The compositions and properties of the polyurethanes prepared as described above are given in

Table I. Composition and molecular weight of the polyesters used

Polyester	Acid ^a /mol%				Diol ^b /mol%			M_n^c
	TA	IA	SSIA	AA	EG	NPG	HD	
A-1	50	50	—	—	50	50	—	2300
A-2	50	48.5	1.5	—	50	50	—	2300
A-3	50	47.5	2.5	—	50	50	—	2400
A-4	50	45	5	—	50	50	—	2300
B-1	—	—	—	100	—	30	70	2000
B-2	—	—	3	97	—	30	70	2000
B-3	—	—	6	94	—	30	70	1900

^a TA, terephthalic acid; IA, isophthalic acid; SSIA, sodium 5-sulfonato-siophthalic acid; AA, adipic acid. ^b EG, 1,2-ethanediol; NPG, 2,2-dimethyl-1,3-propanediol; HD, 1,6-hexanediol. ^c M_n : number-average molecular weight, determined by means of GPC on the basis of polystyrene calibration.

Table II. Characterization of polyurethanes prepared

Polyurethane	Composition/wt			M_n^a	Concn of Na ^b ppm	Specific gravities	T_g^d °C
	Polyester	NPG	MDI				
AR-1	(A-1)/100	7	26.5	22000	0	1.256	81
AR-2	(A-2)/100	7	26.6	26000	920	1.256	
AR-3	(A-3)/100	7	26.6	26000	1800	1.256	82
AR-4	(A-4)/100	7	26.6	25000	3500	1.256	
AL-1	(B-1)/100	7	28.5	25000	0	1.135	
AL-2	(B-2)/100	7	28.5	26000	2200	1.140	−28
AL-3	(B-3)/100	7	28.5	27000	4100	1.145	

^a M_n : number-average molecular weight, determined by means of GPC on the basis of polystyrene calibration. ^b Measured by atomic absorption spectrometry. ^c Specific gravities were given by ups and downs method using CaCl₂ aqueous solution at 25°C according to JIS Z-8807-7. ^d Glass transition temperature (T_g) were measured by differential scanning calorimeter at a temperature raising rate of 20°C min^{−1}.

Table II.

Magnetic Particles and TiO₂. The properties of the magnetic particles and TiO₂ used in this paper are listed in Table III.

Magnetic Paints. The following ingredients were charged into a glass bottle (140 ml). The ingredients were 3 g of polyurethane, 12 g of magnetic particles, 27 g or 37 g of solvent (MEK, toluene, or cyclohexanone), and 40 g of glass beads (2 mmφ). The weight ratio between polyurethane resin and magnetic particle was always 1:4 (wt/wt) in this paper. The glass bottle charged with prescribed ingredients was shaken for 5 h with a paint-shaker (Toyo Seiki Co., Ltd.). The magnetic paint was coated on 50 μm poly(ethylene terephthalate) film with a doctor-blade. The film, thus, obtained was dried at 70°C for 10 min. The thickness of magnetic layer was about 9 μm.

Silicone Oil. Silicone oil (TSF451-10; sp gr, 0.935) was purchased from Toshiba Silicone Co., Ltd.

Measurement

Void Volume Fraction (f_v). A packing degree of magnetic particles in magnetic layer could be estimated from the weight of the silicone oil penetrated into the voids of the magnetic layer. Our method is described below.

(1) A rectangle film was cut out from the magnetic tape, and weighed exactly (W_1).

(2) The film was soaked in silicone oil for 30 min.

(3) After the silicone oil on the surface of the film was wiped off, the film was weighed (W_2).

(4) The magnetic layer was scraped off from the film with sheets of paper containing MEK, and then the film

Table III. Properties of magnetic particles and TiO₂

	Coercive force	Saturated magnetization	Specific surface area	Specific gravity
	Oe	emu g ^{−1}	m ² g ^{−1}	
Metal particle ^a	1612	129.1	57.6	—
Co-adsorbed-γ-Fe ₂ O ₃ ^b	866	77.0	41.2	—
TiO ₂	—	—	23	4.2

^a Supplied by Kanto Denka Co. ^b Supplied by Toda Industry Co.

was weighed exactly (W_3).

(5) Void estimating factor (f_{ev}) in magnetic layer may be defined as eq 1,

$$f_{ev} = W_s / W_{ml} \quad (1)$$

where W_s is the increased weight of the magnetic tape by soaking the tape in silicone oil and W_{ml} is the weight of the magnetic layer. Base film and polyurethane used in this paper do not absorb silicone oil and the magnetic layer can only do. W_s and W_{ml} can be expressed as shown below.

$$W_s = W_2 - W_1, \quad W_{ml} = W_1 - W_3.$$

Surface Properties. Surface properties of magnetic layer were evaluated by gloss and surface roughness. The gloss of magnetic layer was measured by use of gloss meter (Tokyo Denshoku Co., Ltd.) at incident and reflection angle of 60°. Surface roughness was measured by use of surface texture measuring instrument (Tokyo Seimitsu Co., Ltd.). In measurement of surface roughness, 10 points for each sample were measured.

Adsorption Amount of Polyurethane. Magnetic paints were centrifuged at 20000 rpm for 1 h. Polyurethane concentration in the supernatant was measured by gravimetry at 120°C. The adsorption amount of polymer is obtained by

$$A = M_o(C_o - C_e)$$

where A is the adsorption amount of polymer per unit weight of magnetic particles, M_o is the total amount of polymer and solvent per unit weight of magnetic particles, C_o is the initial concentration of polymer, and C_e is the equilibrium concentration of polymer.

RESULTS AND DISCUSSION

A Measuring Method of Void Volume Fraction (f_v)

Silicone oil has low surface tension and easily penetrates into voids in magnetic layer. Polyurethanes used are not soluble in silicone oil. We measured the weight of silicone oil contained in the magnetic layer, and defined the void estimating factor (f_{ev}) as eq 1.

The density (ρ_{ml}) of the magnetic layer is expressed by eq 2

$$\rho_{ml} = W_{ml} / (V_m + V_b + V_v) \quad (2)$$

where W_{ml} is the weight of definite magnetic layer and the sum of weight of the magnetic particles and the binder, and V_m , V_b , and V_v are the volume of the magnetic particles, the binder, and the void in the magnetic layer, respectively. Equation 3 is obtained from eq 2

$$\begin{aligned} 1/\rho_{ml} &= (V_m + V_b)/W_{ml} + V_v/W_{ml} \\ &= 1/C + V_v/W_{ml} \end{aligned} \quad (3)$$

where C is $W_{ml}/(V_m + V_b)$. The C is the density of the magnetic layer without a consideration of the void volume. If the silicone oil penetrates into every void perfectly, V_v is equal to W_s/ρ_{si} where the ρ_{si} is specific gravity of the silicone oil used, and eq 3 is expressed by use of f_{ev} .

$$1/\rho_{ml} = 1/C + f_{ev}/\rho_{si} \quad (4)$$

If the silicone oil penetrates into every void perfectly, the void volume fraction (f_v) is given from eq 1, 2, and 4.

$$\begin{aligned} f_v &= V_v / (V_m + V_b + V_v) = (f_{ev}/\rho_{si})\rho_{ml} \\ &= (f_{ev}/\rho_{si}) / (1/C + f_{ev}/\rho_{si}) \end{aligned} \quad (5)$$

Verification of the Measuring Method. Densities of various magnetic layers and f_{ev} were determined for certifying the relationship between $1/\rho_{ml}$ and f_{ev}/ρ_{si} in eq 4. Figures 1 and 2 show the relationship between f_{ev}/ρ_{si} and $1/\rho_{ml}$ of magnetic layers containing metal particles and Co- γ -Fe₂O₃, respectively. In these experiments, AR-3 and the similar type polyurethanes were used as binder in magnetic layer and the specific gravity of these binder was 1.256 at 25°C. The void fraction was able to be controlled by magnetic particle dispersibility of polyurethane, the dispersion method etc. The densities of magnetic layers were calculated from thickness and weight of magnetic layers with definite area. The relationship between $1/\rho_{ml}$ and f_{ev}/ρ_{si} with 35 points plotted in Figure 1 gave eq 6.

Figure 1. Relationship between $1/\rho_{ml}$ and f_{ev}/ρ_{si} : Magnetic particle, metal; specific gravities of binder, 1.256 at 25°C; magnetic particle/binder, 4/1 (wt/wt).

Figure 2. Relationship between $1/\rho_{ml}$ and f_{ev}/ρ_{si} : Magnetic particle, Co- γ -Fe₂O₃; specific gravities of binder, 1.256 at 25°C; magnetic particle/binder, 4/1 (wt/wt).

$$1/\rho_{ml} = (1.00 \pm 0.03)f_{ev}/\rho_{si} + 0.30 \pm 0.01 \quad (6)$$

In Figure 2, we obtained eq 7.

$$1/\rho_{ml} = (0.92 \pm 0.04)f_{ev}/\rho_{si} + 0.34 \pm 0.02 \quad (7)$$

The slope of these lines in Figures 1 and 2 is 1 or nearly 1 which correspond to the relation given by eq 4.

If silicone oil penetrates into every void perfectly, the value of C in eq 5 can be determined by the measurement of buoyancy of magnetic layer in silicone oil. Using various magnetic tapes composed of PET film and magnetic layer in which AR-3 was used as binder, we calculated the value of C according to eq 8

$$C_1 = W_{ml} / \{ (W_1 - W_{si} - W_h) / \rho_{si} - W_3 / 1.4 \} \quad (8)$$

where C_1 is C value determined by measurement of buoyancy of magnetic layers in silicone oil, W_{si} is the weight of W_1 in silicone oil, W_h is the buoyancy of the

hook and the value of 1.4 is the density of PET film.

The density of magnetic particles was determined by the similar buoyancy method in silicone oil. In order to remove air at surface of magnetic particles, the suspension of magnetic particles in silicone oil was irradiated by supersonic for 30 min. After the suspension was stood for 1 day to sink the magnetic particles, the glass bottle containing the magnetic particles and silicone oil was immersed in silicone oil without scatter of magnetic particles and then was weighted. Table IV shows the results of the measurement of densities of metal particle and Co- γ -Fe₂O₃. These values are in good agreement with those reported by Kondo.¹⁴ Table IV represents the three kinds of C values. Those C values obtained from buoyancy measurement, from eq 6 and eq 7, and from densities of magnetic particles listed in Table IV are similar to each other.

Property of Void in Magnetic Layer

Effect of Thickness of Magnetic Layer and Drying Condition. Silicone oil can not penetrate into the voids which are closed and isolated in the magnetic layer. A close pore might be formed by the shrinking of the magnetic layer during evaporation of solvent. If there are voids between binder polymer forming the adsorbed layer, number of close pore would increase in the case of preparing thick layer and drying at high temperature. As shown in Figure 3 which shows the relationship between void volume fraction (f_v) and the thickness of the magnetic layers, the void volume fraction would be independent of the thickness of magnetic layer.

Table V shows the influence of drying condition on

Table IV. Comparison of C value and density of magnetic particle

Magnetic particle	C Value			Specific gravity of particle from buoyancy
	Buoyancy method	Equation 4	Calculated from specific gravity of particle ^a	
Metal	3.32	3.33	3.31	5.59
Co- γ -Fe ₂ O ₄	2.96	2.94	3.01	4.62

^a $C, (1+k)/(k/\rho_m + 1/\rho_b)$; $k, W_m/W_b$ where W_m and W_b are the weight of magnetic particles and binder; ρ_m , density of magnetic particle; ρ_b , density of binder.

Figure 3. Effect of thickness of magnetic layer on f_v . Magnetic particle, metal; $\square$, binder, AL-2; $\bullet$, binder, AR-3.

the void volume fraction. Drying condition could not influence the void volume fraction.

Effect of Pressure. Magnetic tapes are calendered in order to improve the smoothness of the surface. An effect of pressure treatment on the continuity of void was examined. PET films with magnetic layers were kept for 10 min at 60°C under pressure of 50 kg cm⁻².

The void estimating factor (f_{ev}) gives the void volume fraction (f_v) according to eq 5 from use of the C value calculated from the density of the binder and metal particles. Moreover, the void volume fraction can be calculated from densities of magnetic particles (ρ_m), binder (ρ_b), and magnetic layer (ρ_{ml}) according to eq 9

$$V_v = (V_m + V_b + V_v) - (W_m/\rho_m + W_b/\rho_b)$$

$$V_v/(V_m + V_b + V_v) = 1 - (W_m/\rho_m + W_b/\rho_b)/(W_{ml}/\rho_{ml})$$

$$= 1 - (k/\rho_m + 1/\rho_b)/\{(1+k)/\rho_{ml}\} \quad (9)$$

where W_m and W_b are the weight of definite magnetic particles and binder, respectively, and k is W_m/W_b . Continuity of the void is necessary for silicone oil to penetrate into every void perfectly. But the determination of f_v according to eq 9 does not need the continuity of the void. Table VI shows the effect of pressure on the void volume fraction. In comparison with the void volume fraction according to eq 5 and eq 9, those values were in good agreement. The result suggests that continuity of the void in magnetic layers was kept even after pressing the magnetic layer containing AL-2 that had low T_g (-28°C). After the press treatment, the thickness of the magnetic layer containing AL-2 decreased to about 91% of its initial thickness.

Applying Polymer Layers Containing TiO₂

Magnetic paints are easy to form internal network structure and have particular rheological properties. TiO₂ would give a polymer layer with uniform thickness owing to its good dispersibility into a polymer. When a polymer layer have uniform thickness, the void volume fractions can be calculated according to eq 9. Table VII shows the effect of TiO₂/polyurethane ratio on the void volume fraction (f_v) calculated from the density (ρ_{ml}) of layer or from the void volume fraction determined by using the silicone oil method. Both f_v values are similar to each other, when the ratio of TiO₂/polyurethane became over 6. This silicone oil method was available for polymer layers containing TiO₂, when the pigment volume concentration (PVC) was over 65%. This indicates

Table V. Effect of drying conditions on the void volume fraction^a

Temp	Time	f_v
°C	min	
70	5	0.44
70	10	0.45
70	30	0.45
90	5	0.44
110	5	0.44
130	30	0.46
150	5	0.45

^a Magnetic paint: AL-2/metal particle/MEK/toluene, 3/12/18.5/18.5 wt.

Table VI. Effect of pressure on void fraction^a

Binder ^b		Density of layer	f_v^c	f_{ev}	f_v^d
		g cm ⁻³	Density method		Silicone oil method
AR-3	Before press	1.91	0.42	0.19	0.42
	After press	1.93	0.41	0.18	0.40
AL-2	Before press	1.75	0.44	0.25	0.45
	After press	1.93	0.39	0.20	0.40

^a Press condition: constitution, glass plate/magnetic layer-PET film/polyethylene film (used as cushion)/glass plate; temp, 60°C; time, 10 min; pressure, 50 kg cm⁻². ^b Magnetic paint: AR-3/metal particle/toluene/2-butanone/cyclohexanone, 1/4/4.5/4.5/3.3 wt; AL-2/metal particle/toluene/2-butanone, 1/4/6.2/6.2 wt. ^c Density method: $f_v = 1 - (k/\rho_m + 1/\rho_b)/\{(1+k)/\rho_{ml}\}$; ρ_m , density of magnetic particle; ρ_b , density of binder; ρ_{ml} , density of magnetic layer; k , W_m/W_b where W_m and W_b are the weight of magnetic particles and binder, respectively. ^d Silicone oil method: $f_v = (f_{ev}/\rho_{si})/(1/C + f_{ev}/\rho_{si})$; ρ_{si} , specific gravity of silicone oil; C , $(1+k)/(k/\rho_m + 1/\rho_b)$; $f_{ev} = W_s/W_m$ where W_s is the increased weight of the magnetic tape by soaking the tape in silicone oil and W_m is the weight of the magnetic layer.

Table VII. Void volume fraction of polymer layers containing TiO₂^a

Binder	TiO ₂ /PU ^b ratio	PVC ^c	Density of layer	f_v^d	f_{ev}	f_v^e
	wt/wt	vol%	g cm ⁻³	Density method		Silicone oil method
AR-1	2/1	37	2.21	0.06	0.03	0.07
	4/1	54	2.30	0.20	0.05	0.14
	5/1	60	2.24	0.26	0.06	0.17
	6/1	64	2.27	0.28	0.09	0.23
	7/1	68	2.07	0.36	0.15	0.34
	8/1	71	2.14	0.36	0.17	0.37
	9/1	73	2.02	0.41	0.20	0.42
	10/1	75	2.01	0.42	0.21	0.43
AR-3	2/1	37	2.27	0.03	0.03	0.06
	4/1	54	2.56	0.10	0.02	0.06
	5/1	60	2.62	0.13	0.02	0.06
	6/1	64	2.52	0.20	0.05	0.15
	7/1	68	2.45	0.25	0.08	0.22
	8/1	71	2.52	0.24	0.09	0.24
	9/1	73	2.50	0.27	0.09	0.25
	10/1	75	2.53	0.27	0.12	0.31

^a Coating material: AR-1 or AR-3/TiO₂/2-butanone/toluene/cyclohexanone, composition of solvent, 2-butanone/toluene/cyclohexanone = 36.5/36.5/27 wt. ^b PU: polyurethane. ^c PVC: pigment volume concentration. ^d Density method: $f_v = 1 - (k/\rho_t + 1/\rho_b)/\{(1+k)/\rho_{tl}\}$; ρ_t , density of TiO₂; ρ_b , density of binder; ρ_{tl} , density of layer containing TiO₂; k , W_t/W_b where W_t and W_b are the weight of TiO₂ and binder. ^e Silicone oil method: $f_v = (f_{ev}/\rho_{si})/(1/C + f_{ev}/\rho_{si})$; ρ_{si} , specific gravity of silicone oil; C , $(1+k)/(k/\rho_t + 1/\rho_b)$; $f_{ev} = W_s/W_m$ where W_s is the increased weight of the coated film by soaking the tape in silicone oil and W_m is the weight of the layer containing TiO₂.

that polymer layers containing TiO₂ over the critical pigment volume concentration (CPVC) have continuous voids.

Formation Process of Void

The volume shrink occurs at the time when the magnetic paint forms the magnetic layer. Kanai and Amari⁷ proposed that the structure of the magnetic layers was influenced by the flock structure in the magnetic paints. Magnetic particles seem to work as obstacles at shrink. The presence of obstacles restricts the volume shrink during the solvent volatilization. An increase of cohesive force by the solvent volatilization results in the desorption of binder from magnetic particles owing to the presence of the network structure.

The void of the magnetic layer was as continuous as that of the layer containing many particles of TiO₂ and the continuity of the void was independent of the thickness of the magnetic layer. Even when the polyurethane with low T_g , -28°C, was used as binder, the continuity was kept in spite of the press treatment. These phenomena suggest that magnetic layers are not form-

ed from accumulations of magnetic particles which are covered by the polyurethane. These voids seem to be present not between polyurethanes but between magnetic particles and binder polymer. The voids would be formed during following processes: 1, volatilization of solvent; 2, formation of obstacle by magnetic particles; 3, an increase of cohesion of polymer solution and partial desorption from magnetic particles as Figure 4. Consequently continuous void is formed along with the network structure of magnetic particles.

From our point of view about void-formation process, time of the formation of obstacles and the intensity of interaction between binder polymer and magnetic particles seem to affect void volume fraction of magnetic layer. Time of the formation of obstacles may depend on the steric stabilization by adsorbed polymer, which is similar to colloidal dispersion stability of fine particles having adsorbed polymer layer in organic media.¹⁵ If flocculation of dispersed particles occurs in early stage of formation of magnetic layer, the magnetic layer has much void and rough surface.

If there is strong interaction between binder polymer

Figure 4. Void formation process. —, magnetic particle; $\sim$, polymer in solvent; $\sim$, polymer.

and magnetic particles, magnetic particles may draw near to each other when solvent volatilizes. In this case, the size of networks structure becomes small, so that void volume fraction of magnetic layer decreases.

An Adsorption Behavior of Polyurethanes Having SO_3Na Group

An adsorption behavior of polymers with hydrophilic group have been investigated for binder of magnetic particles. It was found that sulfonic acid^{11,16} and phosphoric acid¹⁷ group had strong interaction with magnetic particles and that the adsorption isotherms of the polymer with such functional groups were those of Langmuir type.

The adsorption behavior of polyurethane having SO_3Na group was similar to that having sulfonic acid or phosphoric acid group as shown in Figure 5. Sodium sulfonate group increased adsorption amount, and the adsorption isotherms were those of the Langmuir type, judging from the linear relationship of Langmuir plots, C_e vs. $C_e A^{-1}$. The adsorption isotherms varied with the kinds of solvents.

Effects of Solvents of Magnetic Paints

When magnetic layer is formed from magnetic paint with thin concentration, shrink rate increases because of an increase of solvent which volatilizes. In dilute magnetic paint, flocculation of dispersed particles are easily

(a) Adsorption isotherm

(b) Langmuir plot

Figure 5. Adsorption isotherm (a) and Langmuir plot (b). ----(□), polyurethane, AR-1, solvent, 2-butanone/toluene (1/1 wt); —(○), polyurethane, AR-3, solvent, 2-butanone/toluene (1/1 wt); —(△), polyurethane, AR-3, solvent, 2-butanone/cyclohexanone (36.5/36.5/27 wt).

Figure 6. Effect of concentration of magnetic paint: magnetic paint, AR-3/Co- γ - Fe_2O_3 (1/4 wt)/solvent. Solvent: —▲ gloss —● f_v , toluene/2-butanone (1/1 wt); —△ gloss —○ f_v , toluene/2-butanone/cyclohexanone (36.5/36.5/27 wt).

formed because of its low viscosity. Figure 6 shows the effect of concentrations on the void volume fraction (f_v) and gloss of magnetic layer, where the concentration means percentage of the sum of magnetic particles and

Table VIII. Effects of solvent of magnetic paints (Binder polyurethane: AR-3)

Magnetic paint ^a		Magnetic layers					
Solvent ^b		Adsorption amount ^d mg g ⁻¹	Polyurethane [η] ^c	Gloss	f_v^f	Surface roughness	Extraction rate ^g
Composition T/B/CH/wt	Values of S_p^c					μm	%
23/23/54	9.5	65	0.34	128	0.45	0.019	41
36.5/36.5/27	9.3	140	0.30	133	0.44	0.019	40
36/64/0	9.2	160	0.25	135	0.46	0.035	34
50/50/0	9.1	170	0.23	35	0.53	0.17	31
55/45/0	9.1	180	0.22	5	0.58	0.32	31

^a Composition of magnetic paints: polyurethane/metal particle/solvent, 1/4/12.3 wt. ^b Solvent: T, toluene; B, 2-butanone; CH, cyclohexanone. ^c SP, solubility parameter; toluene, 8.94; 2-butanone, 9.3; cyclohexanone, 9.92. ^d Calculated by the measurement of polyurethane concentration in the supernatant of magnetic paint by use of centrifuge at 20000 rpm for 1 h. ^e Intrinsic viscosity: measured in respective solvents at 30°C. ^f The void volume fraction: the void volume fraction of magnetic layer was estimated by measurement of the weight increase of magnetic layer by soak into silicone oil. ^g Extraction rate of polyurethane from magnetic layer by soak into 2-butanone/toluene (1/1 wt) for 3 h.

Table IX. Effect of solvent of magnetic paints (Binder polyurethane: AL-2)

Magnetic paint ^a		Magnetic layers					
Solvent ^b		Adsorption amount ^d mg g ⁻¹	Polyurethane [η] ^c	Gloss	f_v^f	Surface roughness	Extraction rate ^g
Composition T/B/CH/wt	Values of S_p^c					μm	%
23/23/54	9.5	75	0.43	123	0.45	0.018	60
36.5/36.5/27	9.3	95	0.39	121	0.46	0.018	60
50/50/0	9.1	110	0.36	124	0.46	0.018	63
61/39/0	9.1	140	0.34	124	0.47	0.017	61
82/18/0	9.0	160	0.26	110	0.41	0.026	63
85/15/0	9.0	180	0.21	96	0.40	0.033	62
91/ 9/0	9.0	210	—	60	0.38	0.044	64

^a Composition of magnetic paints: polyurethane/metal particle/solvent, 1/4/12.3 wt. ^b Solvent: T, toluene; B, 2-butanone; CH, cyclohexanone. ^c SP, solubility parameter; toluene, 8.94; 2-butanone, 9.3; cyclohexanone, 9.92. ^d Calculated by the measurement of polyurethane concentration in the supernatant of magnetic paint by use of centrifuge at 20000 rpm for 1 h. ^e Intrinsic viscosity: measured in respective solvents at 30°C. ^f The void volume fraction: the void volume fraction of magnetic layer was estimated by measurement of the weight increase of magnetic layer by soak into silicone oil. ^g Extraction rate of polyurethane from magnetic layer by soak into 2-butanone/toluene (1/1 wt) for 3 h.

binder polymer in magnetic paint. Co- γ -Fe₂O₃ was used, because metal particle flocculated easily in dilute paint. Effects of concentration varied with the kinds of solvents used in magnetic paints. In 2-butanone/toluene solution, the change of concentration had stronger effect on gloss and f_v than that in 2-butanone/toluene/cyclohexanone solution. Behaviors in two kinds of solvent suggest the difference of the time of formation of flocculation structure.

An adsorption of polymer from solution onto pigments depends strongly on the sort of solvents. It is known that adsorption amount corresponds to the difference of solubility parameters between polymer and solvent, and that polymers are adsorbed on the solid surface with occupied area which is proportional to the size of coil in solution.¹⁰ Specific volume of polymer in solution corresponds to intrinsic viscosity.

Tables VIII and IX show effects of solvents of magnetic paints on properties of magnetic layers and paints. Polyurethanes used as binders for magnetic particles were AR-3 and AL-2 in Tables VIII and IX, respectively. AR-type and AL-type polyurethane differ in polyesterdiol that was used as main material of the polyurethane. The solubility parameters of polyester A-1 and B-1 are 10.5 and 9.66 according to the method of Okitsu.¹⁸ As the solubility parameters of solvents of magnetic paints got near to that of the polyester, the

adsorption amount in magnetic paint decreased, while the properties of surface of the magnetic layer, gloss and roughness, were improved. The properties of surface was settled as the intrinsic viscosity increased. The increase of intrinsic viscosity gave the increase of steric stabilization, delayed the formation of flocculation structure during dry of magnetic paint. Therefore, good solvent gave smooth surface, poor solvent gave rough surface.

There was the opposite relationship between surface roughness and f_v of magnetic layers containing AR-3 or AL-2, as shown in Tables VIII and IX. Judging from the surface roughness, in the case of magnetic paint containing AR-3, the flocculation structure was formed in early stage during dry of magnetic paint, therefore, both surface roughness and f_v greatly increased. On the other hand, in the case of AL-2, the formation of flocculation structure was later than that in the case of AR-3, so that the increase of adsorption amount resulted in the decrease of f_v . There is the case that f_v decreases in spite of the increase of surface roughness.

Effects of SO₃Na Content

Table X shows effects of the concentration of SO₃Na group. The adsorption amount in magnetic paints increased with an increase of the concentration of SO₃Na group. In this case, the increase of adsorption amount gave the decrease of extraction amount of polyurethane

Table X. Effects of SO₃Na content

Polyurethane		Magnetic paint ^a	Magnetic layers			
	Concn of SO ₃ Na ^b	Adsorption amount ^c	Gloss	f_v^d	Surface roughness	Extraction ^e rate
	mequiv kg ⁻¹	mg g ⁻¹			μm	%
AR-1	0	19	11	0.58	0.13	85
AR-2	40	110	121	0.49	0.019	58
AR-3	78	140	133	0.44	0.019	40
AR-4	150	170	144	0.36	0.018	34
AL-1	0	15	3	0.65	0.27	91
AL-2	96	100	125	0.46	0.018	60
AL-3	180	150	123	0.40	0.021	45

^a Composition of magnetic paints: polyurethane/metal particle/toluene/2-butanone/cyclohexanone, 1/4/4.5/4.5/3.3 wt. ^b Calculated by the measurement of Na content. ^c Calculated by the measurement of polyurethane concentration in the supernatant of magnetic paint by use of centrifuge at 20000 rpm for 1 h. ^d The void volume fraction: the void volume fraction of magnetic layer was estimated by measurement of the weight increase of magnetic layer by soak into silicone oil. ^e Extraction rate of polyurethane from magnetic layer by soak into 2-butanone/toluene (1/1 wt) for 3 h.

Table XI. Effects of concentrations of magnetic paints

Magnetic paint ^a			Magnetic layer		
Binder	Solvent ^b	N.V. ^c /wt%	Gloss	f_v^d	Surface roughness/ μm
AR-1	Solv-1	40.5	4	0.60	0.091
		20.8	1	0.60	0.150
	Solv-2	40.5	4	0.57	0.075
		20.8	3	0.56	0.110
AR-2	Solv-1	40.5	106	0.47	0.009
		20.8	65	0.55	0.06
	Solv-2	40.5	101	0.36	0.012
		20.8	106	0.34	0.014
AR-3	Solv-1	40.5	105	0.44	0.010
		20.8	15	0.50	0.18
	Solv-2	40.5	105	0.35	0.012
		20.8	109	0.34	0.021
AR-4	Solv-1	40.5	95	0.45	0.012
		20.8	6	0.49	0.20
	Solv-2	40.5	104	0.36	0.011
		20.8	107	0.32	0.045

^a Composition of magnetic paint: polyurethane/Co- γ -Fe₂O₃/solvent, 1/4/7.3 or 19 wt. ^b Solv-1, 2-butanone/toluene 50/50 wt; Solv-2, 2-butanone/toluene/cyclohexanone 36.5/36.5/27 wt. ^c Non-volatile percentage: (magnetic particle + binder)/(magnetic particle + binder + solvent) $\times$ 100. ^d The void volume fraction: the void volume fraction of magnetic layer was estimated by measurement of the weight increase of magnetic layer by soak into silicone oil.

from magnetic layer by 2-butanone/toluene. Effects of the increase of SO₃Na content remained after solvent volatilization. On the other hand, the increase of adsorption amount in poor solvent had little effect on the extraction amount of polyurethane from magnetic layer. properties of magnetic layers, such as gloss and void volume fraction, improved in connection with the increase the concentration of SO₃Na group.

The influence of concentration of magnetic paint changed in accordance with SO₃Na content and sort of solvent, as shown in Table XI. When the concentration of magnetic paints was turned from 40.5% to 20.8%, the change of surface roughness of magnetic layers was

larger in the case of the layer containing AR-4 than that containing AR-2. In 2-butanone/toluene solution, the decrease of concentration resulted in the increase of void volume fraction. On the other hand, in 2-butanone/toluene/cyclohexanone solution, the decrease of concentration resulted in the decrease of void volume fraction since magnetic particles was well dispersed because of low viscosity. But even in 2-butanone/toluene/cyclohexanone solution, surface roughness of magnetic layer increased in the case of dilute magnetic paint. Behaviors in two kinds of solvent suggest that there is the difference of the time of formation of the flocculation structure according to SO₃Na content. The increase of SO₃Na content furthers formation of the flocculation structure if solvents of magnetic paint are not suitable for binder polymer.

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