Evaluation of Polyurethane Having SO₃Na Group as a Magnetic Binder II. Two-Step Dispersion of Magnetic Particles

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ABSTRACT: Influence of magnetic paint formulations on a packing degree of magnetic particles was studied in the light of interactions of binder polymer and solvent. A method for producing magnetic paint is proposed to decrease the void fraction in magnetic layer. Dispersion in poor solvent gave the magnetic layer with rough surface and with strong interaction between magnetic particles and the binder polymer as well as the magnetic paint with much binder polymer adsorbed onto the magnetic particles. The effects of the dispersion in poor solvent persisted in the final magnetic paint, even though the solvent changed from a poor to good solvent in the second step. In this paper, the two-step dispersion process was investigated in which the first was the dispersion in poor solvent and the second was in good solvent. Binder polymer was added in each step. The decrease of void volume fraction in the magnetic layer was amplified by use of polyurethane with SO₃Na group as a binder polymer in the two-step dispersion method. The decrease of void volume fraction improved the mechanical properties of the magnetic layer.

KEY WORDS Magnetic Tape / Binder / Polyurethane / SO₃Na Group / Void Fraction / Surface Roughness / Two-Step Dispersion / Poor Solvent / Tensile Property /

The presence of void in layers containing fine particles has frequently strong influence on the properties of the layers. Magnetic layers formed from magnetic paint have usually much void volume because of high pigment volume concentration, minute size and needle-like shape of a pigment, and strong interactions between pigments. A packing degree of magnetic particles in the magnetic layer affects not only magnetic and electromagnetic properties,¹ but also mechanical properties of the magnetic layer. A polymer having hydrophilic group increases the intensity of interactions between magnetic particles and the binder polymer, so that the dispersion of magnetic particles is improved in the presence of the polymer having hydrophilic group.^{2,3} Increase of void fraction gives the magnetic layer with rough surface⁴ and decrease of modulus.⁵ Smooth surface is necessary for high density magnetic recording.

Solvents, binder polymers and dispersion machines have influence on the dispersibility and prevention of flocculation of the dispersed particles.⁶ However, there are few papers in respect of the influence of the producing process of magnetic paint on the properties of the magnetic layer such as the void fraction and mechanical properties.

We evaluated polyurethanes having SO₃Na group as a magnetic binder.⁷ Increase of SO₃Na content gave decrease of void fraction, and solvents of magnetic paint affected the properties of magnetic layer. Good solvent for binder polymer gives smooth surface. Poor solvent gives rough surface. But in poor solvent there was decrease of void fraction in spite of increase of surface roughness.⁷

In this paper, we discuss the influence of magnetic paint formulations on a packing degree of magnetic particles in the light of the interaction between binder polymer and solvent. Further, we would like to propose a producing method of magnetic paint to decrease the void fraction in magnetic layer.

EXPERIMENTAL

Materials

Polyurethanes. Polyurethanes having SO₃Na group were synthesized from polyesters containing SO₃Na group, 2,2-dimethyl-1,3-propanediol, and 4,4'-diphenylmethane diisocyanate according to the method in the previous paper.⁷ Polyurethanes having COOH group were synthesized from polyester, 2,2-dimethyl-1,3-propanediol, 2,2-bis(hydroxymethyl)butyric acid (DMBA), and 4,4'-diphenylmethane diisocyanate in toluene/2-butanone solution. DMBA was used to give COOH group to polyurethane. The carboxyl group of DMBA did not react with the isocyanate group in toluene/2-butanone solution under the same conditions as in the previous paper.⁷ The polyesters used for synthesizing polyurethanes and polyurethanes used in this paper are summarized in Tables I and II, respectively.

Magnetic Particles. Metal particles were used in this study. Their properties are listed in the previous paper.⁷

Preparation of Magnetic Paints. Typical procedures for one-step and two-step dispersion are as follows.

One-step dispersion: The following ingredients were charged into a glass bottle (140 ml): 3 g of polyurethane, 12 g of magnetic particles, 37 g of solvent (2-butanone, toluene, or cyclohexanone), and 40 g of glass beads (2 mm ϕ). The glass bottle was shaken for 5 h on a paint-shaker (Toyo Seiki Co., Ltd.).

Two-step dispersion: The following ingredients were first charged into a glass bottle (140 ml): 1.5 g of polyurethane, 12 g of magnetic particles, 18.5 g or 23.5 g of solvent (2-butanone, toluene, or cyclohexanone), and 40 g of glass beads (2 mm ϕ). The glass bottle was shaken for 2.5 h on the paint-shaker. After the further addition of 1.5 g of polyurethane and 18.5 g or 13.5 g of solvent (2-butanone, toluene, or cyclohexanone) to the first suspension, the glass bottle was shaken for 2.5 h on the paint shaker. In the case of two-step dispersion, the first

Table I. Compositions and molecular weights of polyesters used

Polyester	Acid ^a /mol%				Diol ^b /mol%			M_n^c
	TA	IA	SSIA	AA	EG	NPG	HD	
A1	50	50	—	—	50	50	—	2300
A2	50	48.5	1.5	—	50	50	—	2300
A3	50	47.5	2.5	—	50	50	—	2400
A4	50	45	5	—	50	50	—	2300
B1	—	—	—	100	—	30	70	2000
B2	—	—	3	97	—	30	70	2000
B3	—	—	6	94	—	30	70	1900

^a TA, terephthalic acid; IA, isophthalic acid; SSIA, sodium 5-sulfonato-isophthalic 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 GPC based on polystyrene calibration.

Table II. Characterization of the polyurethanes used

Polyurethane	Composition/wt				M_n^c	Concn of Na ^f	Acid value ^g	sp gr ^h
	Polyester ^a	NPG ^b	DMBA ^c	MDI ^d		mequiv kg ⁻¹	mequiv kg ⁻¹	
AR-1	(A1)/100	7	0	26.5	22000	0	3	1.256
AR-2	(A2)/100	7	0	26.6	26000	40	3	1.256
AR-3	(A3)/100	7	0	26.6	26000	78	5	1.256
AR-4	(A4)/100	7	0	26.6	25000	150	8	1.256
AL-1	(B1)/100	7	0	28.5	25000	0	3	1.135
AL-2	(B2)/100	7	0	28.5	26000	96	5	1.140
AL-3	(B3)/100	7	0	28.7	27000	180	5	1.145
AL-4	(B1)/100	5	2	27.3	27000	0	110	1.141
AL-5	(B1)/100	3	4	26.0	29000	0	210	1.135

^a Polyester composition: A-type, terephthalic acid/isophthalic acid/sodium 5-sulfonato-isophthalic acid/1,2-ethanediol/2,2-dimethyl-1,3-propanediol (50/50–45/0–5/50/50, mol%); B-type, adipic acid/sodium 5-sulfonato-isophthalic acid/1,6-hexanediol/2,2-dimethyl-1,3-propanediol (100–94/0–6/70/30, mol%). ^b NPG, 2,2-dimethyl-1,3-propanediol. ^c DMBA, 2,2-bis(hydroxymethyl)butyric acid. ^d MDI, 4,4'-diphenylmethane diisocyanate. ^e M_n : number-average molecular weight, determined by means of GPC on the basis of polystyrene calibration. ^f Measured by atomic absorption spectrometry. ^g Acid value, determined by titrating the polyurethane solution in chloroform with 0.1 equiv potassium ethoxide. ^h Specific gravity was determined by the ups and downs method using CaCl₂ aqueous solution at 25°C according to JIS Z-8807-7.

dispersion was always shaken for 2.5 h.

The ultimate weight ratio between the polyurethane and magnetic particles was always 1:4 in this study.

Measurement

Magnetic Coating. The magnetic paint was coated on the 50 μ m poly(ethylene terephthalate) film with a doctor-blade. This film was dried at 70°C for 10 min. The thickness of the magnetic layer was about 9 μ m.

Void Volume Fraction (f_v). The void volume fraction of magnetic layer was estimated by measurement of the weight increase of the magnetic layer soaked into silicone oil.⁷

Surface Properties. Surface properties of the magnetic layer were evaluated by measuring the gloss at the incident and reflection angle of 60° by use of a gloss meter (Tokyo Denshoku Co., Ltd.).

Contact Angle. Contact angles of the magnetic layer were measured by a static liquid-drop method by a contact angle measuring instrument (Elma Optical Co., Ltd.) at 20°C and 50%RH. Water was used as static liquid drops.

Adsorption Amount. Magnetic paints were centrifuged at 20000 rpm for 1 h. The polymer concentration of the supernatant was measured by gravimetry at 120°C. Adsorption amount of polymer (A) per unit weight of magnetic particles was determined as

$$A = M_0(C_0 - C_e)$$

where M_0 is total amount of polymer and solvent per unit weight of magnetic particles, C_0 is the initial concentration of polymer, and C_e is the equilibrium concentration of polymer.

Ratios of Polyurethanes. The polyurethane ratio in the supernatant of magnetic paint containing polyurethanes, AR-3 and AL-2, was measured by infra-red spectroscopy. The samples of film were obtained by coating the supernatant on polypropylene films. The infra-red spectra of polyurethanes showed the amide-II band of urethane group at 1540 cm⁻¹ and the absorption band of out-of-plane bending of C–H bonds in aromatic polyester at 730 cm⁻¹. The ratio of extinction at 730 cm⁻¹ and 1540 cm⁻¹ was calculated from percentage transmittances. The polyurethane ratio of AR-3 and AL-2 was determined on the base of the calibration line as shown in Figure 1, which related the extinction ratio to the polyurethane ratio in the supernatant.

Mechanical Properties. Mechanical properties of the magnetic layer were evaluated by the tensile strength, tensile elongation, and dynamic modulus. Magnetic layers, about 20 μ m, were formed on polypropylene films easily separated from the magnetic layers. Magnetic paints were coated on polypropylene films and dried at 70°C for 30 min. Tensile strength and elongation at break were measured at 20°C with extension speed of 10 mm min⁻¹ by use of a Tensilon (Toyo Measuring Instruments Co., Ltd.). The temperature dependence of dynamic storage modulus was measured at a frequency

Figure 1. Relationship between polyurethane and extinction ratios: polyurethane ratio, content of AR-3; extinction ratio of infra-red spectrum, extinction at 730 cm^{-1} /extinction at 1540 cm^{-1} .

of 110 Hz by use of a dynamic viscoelastomer (Rheology Co., Ltd.) at a temperature raising rate of $20^\circ\text{C min}^{-1}$.

RESULTS AND DISCUSSION

Influence of Solvents

The adsorption of the polymer from solution onto pigments depends strongly on the sort of solvents. A linear relationship was noted between the maximum adsorption and difference of the solubility parameters (SP) of the polymer and solvent.⁸ Poor solvent for polymer gives much adsorption onto pigments. But much adsorption of polymer does not always result in high packing of pigments.⁷

Table III shows the influence of solvents on the adsorption behavior and properties of the magnetic layer. AR-1 and AR-3 were used as binder polymers, where AR-3 contained SO_3Na group but AR-1 did not. In Table III, the solvents become much poorer from the upper line to the lower line as described in the previous paper.⁷ Influence of solvents on adsorption was evaluated from the extraction rate of polyurethane from the magnetic layer by toluene/2-butanone. The extraction rates from the magnetic layers with AR-3 were between 31 and 40% in spite of the increase of adsorption amount in poor solvents. There was no obvious relationship between the extraction rate and adsorption amount in magnetic paint. For AR-1, the extraction rate decreased with increase of the adsorption amount in magnetic paint. It was likely that the intensity of adsorption corresponded to the adsorption amount in case of the magnetic layer with AR-1. But for AR-3, effects of solvents were not clear from the results of the extraction rate, probably because of the strong interaction of SO_3Na group and magnetic particles.

The contact angles of the magnetic layer with AR-3 varied with the solvent. As shown in Table III, two magnetic layers having AR-1 or AR-3 obtained from the magnetic paints with the most poor solvent, toluene/2-butanone = 64/36 (wt/wt), had the same contact angle regardless of the presence or absence of the SO_3Na group. The contact angles of the magnetic layers with

AR-3 decreased as the solvents of magnetic paints became better for AR-3. Kotera *et al.*⁹ reported that contact angles of the film formed from polyesters containing SO_3Na group became smaller with increase of the SO_3Na content at the film surface. If the decrease of contact angles results from the SO_3Na group that does not adsorb onto magnetic particles, it would be considered that SO_3Na group effectively adsorbs onto magnetic particles in poor solvent. There was little change of contact angle of the magnetic layer with AR-3 after the soaking into toluene/2-butanone. This seems that the adsorbed AR-3 in the magnetic layer does not desorb by the soak. In case of AR-1, the contact angle after soaking into toluene/2-butanone was measured only using the most poor solvent, toluene/2-butanone = 64/36 (wt/wt), as the solvent of magnetic paint. Even after soaking treatment, the adsorbed AR-1 from poor solvent seemed to remain on the magnetic particles similar to that of the adsorbed AR-3. It was likely that the strength of adsorption of the polyurethane, AR-1, onto magnetic particles increased by the dispersion in poor solvent because the adsorbed polyurethane did not desorb easily.

Effects of solvents on adsorption strength were examined by two-step dispersion in which the displacement of adsorbed polymers was evaluated. Table IV shows the properties of magnetic paints and magnetic layers obtained by two-step dispersion. Either AR-1 or AR-3 was used as a binder polymer in each step. The final compositions of exptl (A), (B), (C), and (D) were identical, but properties of magnetic paints and magnetic layers were different. In exptl (C), there were small adsorption amount in magnetic paints and little Na concentration in the supernatant obtained by centrifugation at 20000 rpm for 1 h. This suggests that the second dispersion with AR-1 (SO_3Na -free polyurethane) does not displace the AR-3 (polyurethane having SO_3Na group) adsorbed. AR-3 exclusively adsorbed and prevented AR-1 from adsorption onto magnetic particles in case of the one-step dispersion, exptl (D), and the two-step dispersion, exptl (C), as described above. Miscibility between the polyurethane having SO_3Na group and SO_3Na -free polyurethane decreases with increase of SO_3Na content. Bad miscibility between AR-1 and AR-3 seems for AR-3 to prevent AR-1 from adsorption onto magnetic particles.

On the other hand, there was increase of adsorption amount and Na concentration in the supernatant of magnetic paints in case of exptl (A) and (B) in which AR-1 was firstly dispersed. The first adsorbed polymer, AR-1, was not perfectly removed from magnetic particles by the dispersion with AR-3. The adsorption amount of AR-1 increased particularly in exptl (A). This corresponds to the result in Table III, that the polyurethane adsorbed onto magnetic particles in poor solvent does not desorb easily. In spite of the decrease of SO_3Na group, the void fraction in the magnetic layer from exptl (A) was smaller than that of the magnetic layer obtained by one-step dispersion with only AR-3 as shown in Table III. The solvent used at the first dispersion of exptl (A) was poorer for AR-1 than that of exptl (B). Effects in the first dispersion, especially solvent effects remained in final magnetic paint.

Table III. Effects of solvents

Magnetic paint ^a						Properties of magnetic layers				
Binder	Solvent			SP ^c value	Adsorption amount ^d mg g ^{−1}	Gloss	<i>f_v</i> ^e	Extraction rate ^f %	Contact angle ^g /deg	
	Composition ^b /wt%								Before extractopm	After extraction
	T	B	CH							
AR-1	36.5	36.5	27	9.3	19	11	0.58	85	65	* ^h
	50	50	—	9.1	64	4	0.67	76	64	* ^h
	64	36	—	9.1	80	2	0.66	71	62	61
AR-3	36.5	36.5	27	9.3	140	133	0.44	40	53	55
	50	50	—	9.1	170	35	0.53	31	56	58
	64	36	—	9.1	185	3	0.60	38	62	61

^a Composition of magnetic paint: polyurethane/solvent/metal particles, 1/12.3/4 (wt). ^b T, toluene; B, 2-butanone; CH, cyclohexanone. ^c Solubility parameter: toluene, 8.94; 2-butanone, 9.3; cyclohexanone, 9.92. ^d Calculated from polyurethane concentration in the supernatant of magnetic paint obtained by centrifugation at 20000 rpm for 1 h. ^e Void volume fraction: the void volume fraction of magnetic layer estimated from the weight increase of magnetic layer by soaking into silicone oil. ^f The extraction rate of polyurethane by the soak into toluene/2-butanone (50/50, wt) at 3 hours at 20°C; extraction rate, $(5W_e/W_{ml}) \times 100$ (%) where W_e is the weight decrease of magnetic tape by soaking and W_{ml} is the weight of the magnetic layer. ^g The contact angles of magnetic layers were measured by the static water-drop method at 20°C before and after soaking in toluene/2-butanone (50/50, wt) for 3 hours.

Table IV. Effects of solvents in the two-step dispersion (I)

Exptl	Magnetic paint ^a														Magnetic layer			
	First dispersion							Second dispersion							Adsorption amount ^d mg g ⁻¹	Concn of Na ^e of polyurethane in supernatant mg kg ⁻¹	Gloss	<i>f</i> _v ^f
	Binder	Composition ^b /wt					SP ^c of solvent	Binder	Composition ^b of additives/wt									
		Pu	T	B	CH	Metal			Pu	T	B	CH						
(A)	AR-1	0.5	3.9	2.3	—	4	9.1	AR-3	0.5	0.6	2.3	3.3	9.3	110	92	136	0.32	
(B)	AR-1	0.5	3.9	3.9	3.3	4	9.3	AR-3	0.5	0.6	0.6	—	9.3	95	60	112	0.45	
(C)	AR-3	0.5	3.9	3.9	3.3	4	9.3	AR-1	0.5	0.6	0.6	—	9.3	62	3.9	38	0.54	
(D)	one-step dispersion AR-1/AR-3/T/B/CH/Metal 0.5/0.5/4,5/4,5/3.3/4										9.3	66	4.4	31	0.58			

^a Final composition of magnetic paint: polyurethane/toluene/2-butanone/cyclohexanone/metal particles, 1/4.5/4.5/3.3/4 (wt). ^b Pu, polyurethane; T, toluene; B, 2-butanone; CH, cyclohexanone. ^c Solubility parameter: toluene, 8.94; 2-butanone, 9.3; cyclohexanone, 9.92. ^d Calculated from polyurethane concentration in the supernatant of magnetic paint obtained by centrifugation at 20000 rpm for 1 h. ^e Measured by atomic absorption spectrometry. ^f Void volume fraction: void volume fraction of magnetic layer estimated from the weight increase of magnetic layer by soaking in silicone oil.

Two-Step Process with Dispersion in Poor Solvent

Influence of Solvents at the First Dispersion. To make use of the adsorption behavior in poor solvent, we examined the two-step dispersion which has the first dispersion process with a poor solvent and the second dispersion process with a good solvent. The properties of solvent for binder polymer changed from poor to good by addition of another solvent into the suspension. Table V (AR-3) and Figure 2 (AL-2) show the influence of solvents in the first dispersion. The final compositions of magnetic paints in Table V and Figure 2 were AR-3/toluene/2-butanone/cyclohexanone/metal particles (1/4.5/4.5/3.3/4, wt) and AL-2/toluene/2-butanone/metal particles (1/6.2/6.2/4, wt), respectively. Compositions of solvents were finally same but different at the first dispersion. In comparison with exptl (E), (F), and (G), as SP values of solvents at the first dispersion lowered, namely the solvents became poorer for AR-3, the properties of surface and packing degree of the magnetic layer improved. The void volume fraction in exptl (E)

especially decreased to about 40% the same as that in exptl (J) obtained from one-step dispersion method. In comparison with exptl (E), (H), and (I), the divided addition of the binder polymer was effective to improve smoothness and packing degree of the magnetic layer.

Figure 2 shows the effect of toluene/2-butanone ratio at the first dispersion on the gloss and the void volume fraction (f_v) of the magnetic layer. Solubility of AL-2 in toluene/2-butanone decreases as the ratio of toluene increases. AL-2 is not completely soluble as the ratio of toluene/2-butanone is over 90/10 (wt/wt). Properties of the magnetic layer were improved by the two-step dispersion which contained the first dispersion process with poor solvent. The use of toluene/2-butanone (1/1, wt) in the first dispersion gave the magnetic layer with the same properties as that⁷ from the one-step dispersion in toluene/2-butanone (1/1, wt). Therefore the effects of this two-step dispersion method does not result from mere division of the dispersion process.

Influence of SO₃Na Concentration. It appeared that

Table V. Effects of solvents in the two-step dispersion (2)

Exptl	Magnetic paint ^a													Magnetic layer		
	First dispersion							Second dispersion						Adsorption amount ^d mg g ⁻¹	Gloss	<i>f_v</i> ^e
	Binder	Composition ^b /wt					SP ^c of solvent	Binger	Composition ^b of additives/wt				SP ^c of solvent			
		Pu	T	B	CH	Metal			Pu	T	B	CH				
(E)	AR-3	0.5	3.9	2.3	—	4	9.1	AR-3	0.5	0.6	2.3	3.3	9.3	138	165	0.18
(F)	AR-3	0.5	2.6	2.6	2	4	9.3	AR-3	0.5	1.9	1.9	1.3	9.3	123	149	0.40
(G)	AR-3	0.5	0.6	2.3	3.3	4	9.6	AR-3	0.5	3.9	2.3	—	9.3	113	130	0.45
(H)	AR-3	1	4.5	2.8	—	4	9.1	—	—	—	1.7	3.3	9.3	125	144	0.34
(I)	AR-3	1	4.5	4.5	—	4	9.1	—	—	—	—	3.3	9.3	122	147	0.32
(J)	One-step dispersion AR-3/T/B/CH/Metal 1/4.5/4.5/3.3/4												9.3	140	133	0.44

^a Final composition of magnetic paint: polyurethane/toluene/2-butanone/cyclohexanone/metal particles, 1/4.5/4.5/3.3/4 (wt). ^b Pu, polyurethane; T, toluene; B, 2-butanone; CH, cyclohexanone. ^c Solubility parameter: toluene, 8.94; 2-butanone, 9.3; cyclohexanone, 9.92. ^d Calculated from polyurethane concentration in the supernatant of magnetic paint obtained by centrifugation at 20000 rpm for 1 h. ^e Void volume fraction: void volume fraction of magnetic layer estimated from the weight increase of magnetic layer by soaking in silicone oil.

Figure 2. Effects of solvent in the first dispersion: final composition of magnetic paint, AL-2/toluene/2-butanone/metal particles (1/6.2/6.2/4, wt); composition at the first dispersion, AL-2/toluene/2-butanone/metal particles (0.5/5.6–0.6/0.6–5.6/4, wt).

SO₃Na group effectively adsorbed on magnetic particles in poor solvent as shown in Table III. Figures 3 and 4 show the influence of SO₃Na concentration in the two-step dispersion. The final compositions of magnetic paints in Figures 3 and 4 were AR-type polyurethane/toluene/2-butanone/cyclohexanone/metal particles (1/4.5/4.5/3.3/4, wt) and AL-type polyurethane/toluene/2-butanone/cyclohexanone/metal particles (1/7.8/1.2/3.3/4, wt), respectively. The compositions at the first dispersion in Figures 3 and 4 were AR-type polyurethane/toluene/2-butanone/metal particles (0.5/3.9/2.3/4, wt), and AL-type polyurethane/toluene/2-butanone/metal particles (0.5/7.2/0.6/4, wt), respectively, in which solvents were poorer than those in the final stage. AR-4 and AL-3 were not completely soluble in the solvents used at the first dispersion. Properties of the magnetic layer, particularly void volume fraction, were improved by use of this two-step dispersion method in comparison with those by the one-step dispersion method. We pointed out that increase of interaction between magnetic particles and binder polymer decreases the void volume fraction.⁷ The SO₃Na group effectively worked by use of the two-step dispersion method which con-

Figure 3. Influence of SO₃Na in the two-step dispersion: Final composition of magnetic paint, AR-polyurethane/toluene/2-butanone/cyclohexanone/metal particles (1/4.5/4.5/3.3/4, wt); composition at the first dispersion in two-step dispersion, AR-polyurethane/toluene/2-butanone/metal particles (0.5/3.9/2.3/4, wt); —□, (gloss); —■, (f_v), two-step dispersion; —△, (gloss); —▲, (f_v), one-step dispersion.

Figure 4. Influence of SO₃Na in the two-step dispersion: final composition of magnetic paint, AL-polyurethane/toluene/2-butanone/cyclohexanone/metal particles (1/7.8/1.2/3.3/4, wt); composition in the first dispersion, AL-polyurethane/toluene/2-butanone/metal particles (0.5/7.2/0.6/4, wt); —□, (gloss); —■, (f_v), two-step dispersion; —△, (gloss); —▲, (f_v), one-step dispersion.

Table VI. Effects of dispersion time

Exptl	Magnetic paint ^a														Magnetic layer			
	First dispersion ^b							Second dispersion				SP ^d of solvent	Time of second dispersion	Adsorption amount ^e	Ratio ^f of AR-3/Al-2 in supernatant	Gloss	<i>f_v</i> ^g	
	Binder	Composition ^c /wt					SP ^d of solvent	Binder	Composition ^c of additives/wt									
		Pu	T	B	CH	Metal			Pu	T	B							CH
													min	mg g ^{−1}	wt			
(K)	AR-3	0.5	3.9	2.3	—	4	9.1	AL-2	0.5	0.6	2.3	3.3	9.3	150	115	37/63	173	0.22
														750	87	44/56	173	0.20
(L)	AL-2	0.5	5.6	0.6	—	4	9.0	AR-3	0.5	0.6	5.6	—	9.1	150	131	52/48	167	0.29
														750	109	51/49	161	0.25
(M)	One-step dispersion	AR-3/AL-2/T/B/CH/Metal	0.5/0.5/4.5/4.5/3.3/4										9.3	300 ^h	114	42/58	124	0.47
														900 ^h	85	49/51	141	0.42
(N)	One-step dispersion	AR-3/AL-2/T/B/Metal	0.5/0.5/6.2/6.2/4											300 ^h	137	46/54	130	0.45
														900 ^h	105	47/53	139	0.44

^a Final compositions of magnetic paints: polyurethane/solvent/metal particle, 1/12.3/4 (wt). ^b First dispersion time, 150 min. ^c Pu, polyurethane; T, toluene; B, 2-butanone; CH, cyclohexanone. ^d Solubility parameter: toluene, 8.94; 2-butanone, 9.3; cyclohexanone, 9.92. ^e Calculated from polyurethane concentration in the supernatant of magnetic paint obtained by centrifugation at 20000 rpm for 1 h. ^f The ratio of AR-3/AL-2 was measured by use of a infra-red spectroscopy. ^g Void volume fraction: void volume fraction of magnetic layer estimated from the weight increase of magnetic layer by soaking in silicone oil. ^h Time of one-step dispersion.

tained the first dispersion process with poor solvent.

Influence of Dispersion Time. Table VI shows the influence of the second dispersion time in the two-step dispersion without change of the first dispersion time. Two polyurethanes, AR-3 and AL-2 both possessing the SO₃Na group, were used as binder polymers. Exptl (K) and exptl (L) have the same composition as exptl (M) and exptl (N), respectively. In the solvent used in Table VI, the adsorption amount of AR-3 was more than that of AL-2.⁷ Longer dispersion time led to lower adsorption amount both in the two-step and in the one-step dispersion. The ratio of AR-3/AL-2 in the supernatant of magnetic paints indicated that the adsorption amount of the binder polymer in the first dispersion with poor solvent was more than that in the second dispersion with good solvent. The adsorption amount varied with the second dispersion time, but the adsorption superiority of the binder polymers was independent of dispersion time. As shown in Table VI, the two-step dispersion method was effective irrespective of the second dispersion time.

Comparison of COOH and SO₃Na Group. It is found that COOH group is effective to increase interactions between binder polymer and magnetic particles.¹⁰ Figure 5 shows the gloss and void fraction of the magnetic layer with polyurethanes having the COOH group. Polyurethanes, AL-1, AL-4, and AL-5, used in Figure 5 were made from aliphatic polyester. AL-4 and AL-5 are similar to AL-1 except for high COOH content. There was the effect of the two-step dispersion on the gloss and void fraction of the magnetic layer. However, in comparison with Figure 4, COOH group did not amplify the effect of the two-step dispersion. It probably resulted from the solubility in the solvent at the first dispersion. AL-3 which contains SO₃Na group was not completely

Figure 5. Influence of COOH group in the two-step dispersion: final composition of magnetic paint, AL-1,4 or 5/toluene/2-butanone/cyclohexanone/metal particles (1/7.8/1.2/3.3/4, wt); composition in the first dispersion, AL-1,4 or 5/toluene/2-butanone/metal particles (0.5/7.2/0.6/4, wt); —□, (gloss); —■, (f_v), two-step dispersion; —△, (gloss); —▲, (f_v), one-step dispersion.

soluble in the solvent used at the first dispersion, but AL-5 having no SO₃Na group was soluble in the solvent used at the first dispersion at 10 wt% solution. It appears that the decrease of solubility by SO₃Na group improves the dispersibility in the two-step dispersion method.

Mechanical Properties of Magnetic Layer

A degree of void volume affects the mechanical properties of the magnetic layer. Table VII and Figure 6 show tensile properties and dynamic storage modulus of the magnetic layer. Both AR-type and AL-type poly-

Table VII. Properties of the magnetic layer

Exptl	Magnetic paint ^a												Magnetic layer				
	First dispersion							Second dispersion					Gloss	f_v^d	Tensile strength ^e kg mm ⁻²	Elongation ^e %	
	Binder	Composition ^b /wt					SP ^c of solvent	Binder	Composition ^b of additives/wt								Sp ^c of solvent
		Pu	T	B	CH	Metal			Pu	T	B	CH					
(K)	AR-3	0.5	3.9	2.3	—	4	9.1	AL-2	0.5	0.6	2.3	3.3	9.3	173	0.22	1.9	6.7
(O)	AL-2	0.5	5.6	0.6	—	4	9.0	AR-3	0.5	0.6	0.6	5	9.4	165	0.27	2.3	2.5
(P)	AR-4	0.5	3.9	2.3	—	4	9.1	AL-3	0.5	0.6	2.3	3.3	9.3	161	0.21	1.9	4.0
(Q)	AL-3	0.5	5.6	0.6	—	4	9.0	AR-4	0.5	0.6	0.6	5	9.4	178	0.15	2.6	2.7
(R)	AR-3	0.5	2.3	2.3	1.7	4	9.3	AL-2	0.5	2.3	2.3	1.7	9.3	146	0.34	1.7	1.3
(S)	AL-2	0.5	2.3	2.3	1.7	4	9.3	AR-3	0.5	2.3	2.3	1.7	9.3	118	0.43	1.4	1.0
(M)	One-step dispersion	AR-3/AL-2/T/B/CH/Metal 0.5/0.5/4.5/4.5/3.3/4											9.3	124	0.47	1.1	1.0
(T)	One-step dispersion	AR-3/AL-2/T/B/CH/Metal 0.5/0.5/6.2/1.2/5/4											9.4	123	0.45	1.3	1.3
(U)	One-step dispersion	AR-4/AL-3/T/B/CH/Metal 0.5/0.5/4.5/4.5/3.3/4											9.3	132	0.42	1.3	2.0
(V)	One-step dispersion	AR-4/AL-3/T/B/CH/Metal 0.5/0.5/6.2/1.2/5/4											9.4	134	0.41	1.2	2.7

^a Final composition of magnetic paint: polyurethane/solvent/metal particles, 1/12.3/4 (wt). ^b Pu, polyurethane; T, toluene; B, 2-butanone; CH, cyclohexanone. ^c Solubility parameter: toluene, 8.94; 2-butanone, 9.3; cyclohexanone, 9.92. ^d Void volume fraction: void volume fraction of magnetic layer estimated from the weight increase of magnetic layer by soaking in silicone oil. ^e Mechanical properties of magnetic layer measured at extension speed of 10 mm min⁻¹ at 20°C.

Table VIII. Tensile properties of polyurethane

Polyurethane	Tensile strength ^a	Tensile elongation ^a
	kg mm ⁻²	%
AR-3	6.8	6
AL-2	0.1	950

^a Measured at 20°C at extension speed of 200 mm min⁻¹.

urethane were used as binder polymers to evaluate the influence of the formulation on mechanical properties. Both polyurethanes have different mechanical properties as shown in Table VIII. AR-type polyurethanes, whose glass transition temperatures are about 80°C, have high tensile strength, 6–7 kg mm⁻², and low elongation, 5–7%; AL-type polyurethanes, whose glass transition temperatures are about –30°C, have low tensile strength less than 0.2 kg mm⁻², and high elongation more than 800% at 20°C with extension speed of 200 mm min⁻¹. The two-step dispersion method with the first dispersion in poor solvent, exptl (K), (O), (P), and (Q), gave a tough magnetic layer with low void volume fraction in comparison with the one-step dispersion, exptl (M), (T), (U), and (V). The two-step dispersion method with same solvent in the first and second dispersions, exptl (R) and (S), gave a brittle magnetic layer with high void volume fraction in comparison with that of exptl (K), which had the first dispersion in the poor solvent.

Figure 6 shows the temperature dependence of dynamic storage modulus of the magnetic layer. The moduli of magnetic layers from the two-step dispersion corresponding to exptl (K) and (Q) in Table VII, were higher than those of the one-step dispersion corresponding to exptl (M) and exptl (V) in Table VII. The increase of these moduli of magnetic layers was related to the

Figure 6. Temperature dependence of dynamic storage modulus of magnetic layer and clear film: —●, two-step dispersion, AL-3/toluene/2-butanone/metal particles (0.5/5.6/0.6/4, wt) → AR-4/toluene/2-butanone/cyclohexanone (0.5/0.6/0.6/5, wt); —▲, two-step dispersion, AR-3/toluene/2-butanone/metal particles (0.5/3.9/2.3/4, wt) → AL-2/toluene/2-butanone/cyclohexanone (0.5/0.6/2.3/3.3, wt); —●, one-step dispersion, AL-3/AR-4/toluene/2-butanone/cyclohexanone/metal particles (0.5/0.5/6.2/1.2/5/4, wt); —▲, one-step dispersion, AL-2/AR-3/toluene/2-butanone/cyclohexanone/metal particles (0.5/0.5/4.5/4.5/3.3/4, wt); ---○, clear film of AL-3/AR-4 (1/1 wt); ---△, clear film of AR-3/AL-2 (1/1 wt).

decrease of void volume fraction.

When the solvent at the first dispersion was poorer than the final solvent, the adsorption of binder polymer in the first dispersion had priority over the adsorption of the binder polymer in the second dispersion as shown by comparison of the ratio of AR-3 and AL-2 in the supernatant of exptl (K) and exptl (L) in Table VI. On tensile property of the magnetic layer, the influence of

binder polymer that was initially adsorbed to magnetic particles was smaller than that of the secondly adsorbed binder polymer, because the tensile strengths of exptl (O) and exptl (Q), in which AR-type polyurethanes having high tensile strength were adsorbed in the second dispersion, were higher than those of exptl (K) and exptl (P), respectively, as shown in Table VII. Therefore, if the abilities of adsorption of two binder polymers is same, the tensile properties of magnetic layer are strongly affected by the binder polymers used in the second dispersion.

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