

Functional Polymers for Colloidal Applications. X. Syntheses of Graft-Charged Naphthalene–Formaldehyde Condensates and Their Ability to Disperse Dyes

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SYNOPSIS

N-(3-sodium propylsulfonate)- α -naphthylamine–formaldehyde condensates (NAFS) and *O*-(3-propylsulfonate)- α -naphthol–formaldehyde condensates (NOFS) are synthesized by condensation reactions followed by ring-opening reactions. Those condensates are used as dispersants to disperse dyes in water (C.I. Navy Blue 79 and C.I. Brown 1), and can be compared to the conventional dispersants [e.g., naphthalenesulfonate–formaldehyde condensates (NSF)]. The dispersing properties of the condensates were evaluated by scanning electron microscopy (SEM), sedimentation, as well as measurements of viscosity. For NAFS or NOFS, the sulfonate groups were grafted separately on the backbone of the condensate; however, for NSF, the sulfonate groups were anchored on the backbone of the condensate. The structural effects of those condensates were demonstrated by comparing the dispersing ability of these condensates, and the conventional condensates NAFS and NOFS exhibit better dispersing abilities than NSF for the Navy Blue 79 and Brown 1 dyes. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Dispersing technology has been widely applied in diverse industries^{1–3} such as coatings, pigments, agriculture, magnetic tape, and photographic film.⁴ The technology has widely attracted attention both for academic studies and industrial applications. When particles are dispersed in solution, the system is thermodynamically unstable; thus, dispersants are normally added to stabilize the system. The main function of the dispersant is to provide the particles with an electrostatic barrier⁵ and/or with steric hindrance⁶ to prevent the coagulation of the particles.

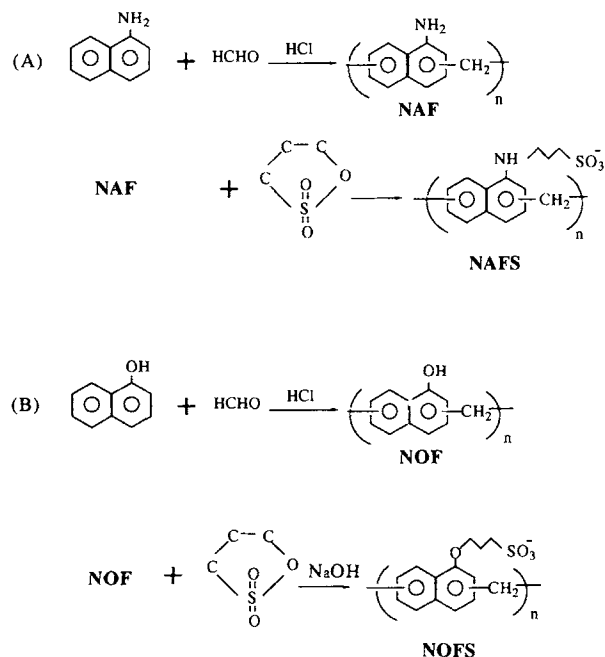
Dispersants can be divided into three types: surfactants, oligomers, and polymers. Representative examples of oligomers, which are used as industrial dispersants, are the naphthalenesulfonate–formal-

dehyde condensates (NSF). Due to the strong adsorption of NSF onto polar and nonpolar surfaces, the NSFs have been widely used to disperse dyes, coal, and cement in aqueous systems.^{7–11} The adsorption of NSF on polar surfaces (e.g., dye and cement particle) mainly arises from the interaction between the polarizable naphthalene ring and the polar surface.¹²

According to the DLVO theory,¹² for a dispersed system, a higher repulsive potential energy (V_r) results in a higher total potential energy barrier, which more efficiently prevents the coagulation of two particles. In turn, a higher effective thickness ($1/\kappa$) of an adsorption layer results in a higher repulsive potential energy both for the case of $(1/\kappa) \gg a$ or $(1/\kappa) \ll a$, where a is the radius of the particle.

For the conventional NSF dispersant, the SO_3Na group is anchored on the naphthalene ring. If the SO_3Na group is grafted onto but separated away from the naphthalene ring, instead of being anchored on the ring, the effective thickness of the adsorption

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Scheme 1 The synthesis procedure for (A) *N*-(3-sodium propylsulfonate)- α -naphthylamine-formaldehyde condensate (NAFS) and (B) *O*-(3-propylsulfonate)- α -naphthol-formaldehyde condensate (NOFS).

layer will be increased, and consequently, it can be expected to act as a more efficient dispersant.

In this study, different types of naphthalene-formaldehyde condensates were synthesized by grafting different types of sulfonate groups (NAFS and NOFS) onto the naphthalene ring, and their efficiency to disperse dyes has been investigated by viscosity, sedimentation, and scanning electron microscopy methods. Those results are compared with those obtained with conventional NSF dispersants to demonstrate the effect of separating the sulfonate group away from the naphthalene ring on the ability to disperse dyes.

EXPERIMENTAL

Materials

α -Naphthylamine (Fluka), α -naphthol (Fluka), formaldehyde solution (Merck, 37 wt %, EP Grade), and propane sultone (Tokyo Kasei, GR Grade) were used without further purification. Commercial high and low molecular weight NSF dispersants (Lomar D and Lomar PW, respectively, Henkel) were also used as dispersants for comparison. C.I. Navy Blue 79 (E-Hwa Co., with a BET surface area of 4.85

$\pm 0.03 \text{ m}^2/\text{g}$), and C.I. Brown 1 (E-Hwa Co., with a BET surface area of $1.53 \pm 0.04 \text{ m}^2/\text{g}$) were used as supplied. The water used in these experiments was ion exchanged and distilled, with a pH value between 6.8–7.2 and a conductivity of $4.4 \pm 10^{-6} \text{ W}^{-1}\text{m}^{-1}$.

Methods

Synthesis and Characterization of Condensates

Synthesis of *N*-(3-sodium propylsulfonate)- α -naphthylamine-Formaldehyde Condensates (NAFS) [Scheme 1(A)]. Formaldehyde (10 wt %, 84.6 g) was added to a mixture of α -naphthylamine (42.9 g) and HCl (5 wt %, 65.9 g). The reactor was heated at 95°C for 4 h. The temperature was then decreased to $60\text{--}70^\circ\text{C}$, and an aqueous solution of NaOH (20 wt %, 18 g) was added to neutralize the HCl. The mixture was washed with water, and the insoluble fraction was separated from the aqueous phase by filtration, and was then dissolved under stirring in a mixed solvent comprised of 90% phenol and 10% acetone (180 g). To this solution, propane sultone (73.5 g) was added dropwise, and the temperature was increased to $70\text{--}80^\circ\text{C}$ and reacted for 10 h. After reaction, the mixture was precipitated with acetone. The precipitate was dissolved in water and the pH value of the solution was adjusted to 9–10. The water was evaporated, and the precipitation process was repeated in acetone once again to obtain the product (NAFS) (72.2 g).

Synthesis of *O*-(3-sodium propylsulfonate)- α -naphthol-formaldehyde condensates (NOFS) [Scheme 1(B)]. Formaldehyde (3 wt %, diluted to 240 g) was added to a mixture of α -naphthol (43.2 g) and HCl (5 wt %, 65.7 g) in a 500 mL reaction kettle. Condensation ring-opening reaction with propane sultone (43.9 g) and purification were conducted with the above-mentioned processes, and similar conditions of preparing NAFS. The purified product (NOFS) (76.4 g) was obtained.

The reaction conditions for synthesizing NAFS and NOFS are summarized in Table I.

Characterization of Condensates. The reprecipitated NAFS and NOFS were dissolved in D_2O and characterized by $^1\text{H-NMR}$ (Bruker WP 100). For NAFS and NOSF (Figs. 1 and 2, respectively), the protons on the naphthalene ring appeared at $\delta = 6.5\text{--}8.0 \text{ ppm}$; the methylene group between two benzene rings was found at $\delta = 4.0\text{--}4.5 \text{ ppm}$,^{13,14} and the other methylene groups $\text{--N}(\text{CH}_2)_3\text{--}$ or $\text{--O}(\text{CH}_2)_3\text{--}$

Table I Reaction Condition for Synthesizing the NFS-Type Dispersants

Dispersant	HCHO/Monomer/HCl (Molar Ratio)	Reaction Time (h)	
		Condensation ^a	Opening ^b
NAFS	0.91/1.0/0.3	10.0	10.0
NOFS	0.8/1.0/0.3	4.0	5.0

^a The reacted temperature was maintained at 95°C.

^b The reaction temperature for the ring opening of propane.

were distributed at 1.8–3.8 ppm.^{14,15} Molecular weight distributions of NAFS (sodium salts) and NOFS obtained were compared by the GPC method^{16,17} (Table I). Two GPC columns (Waters Ultrahydrogel-120 and 250, with a length of 30 cm and an inner diameter of 7.8 mm, using fully porous and highly crosslinked hydroxylated polymer as packing material) were combined in series for the measurements. Water (GPC grade) was used as the mobile phase.

Assessments of the Dispersing Abilities of the Condensates

The dyes (C.I. Brown 1 and C.I. Navy Blue 79) were dispersed in water by using the different types of dispersants (i.e., NAFS, NOFS, NSF-H, and NSF-L) following the formulation shown in Table II. For example, a given dispersant was dissolved in water

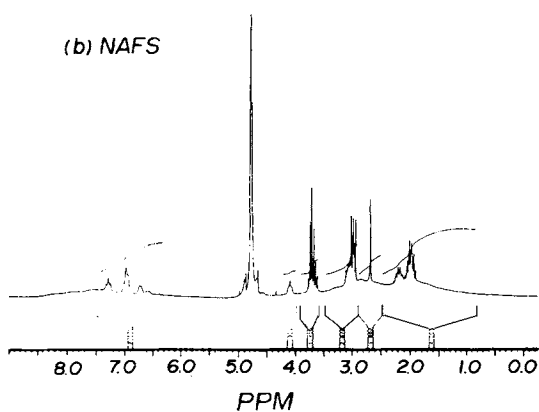
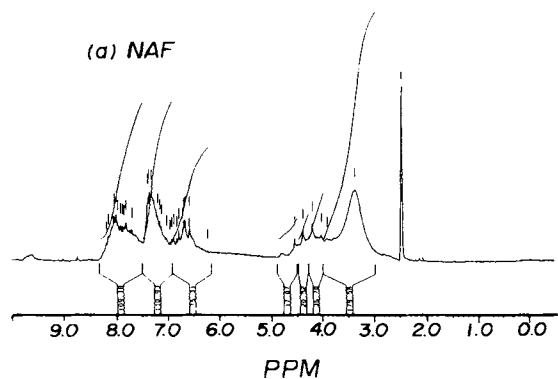


Figure 1 (a) ¹H-NMR spectra for NAF; (b) ¹H-NMR spectra for NAFS.

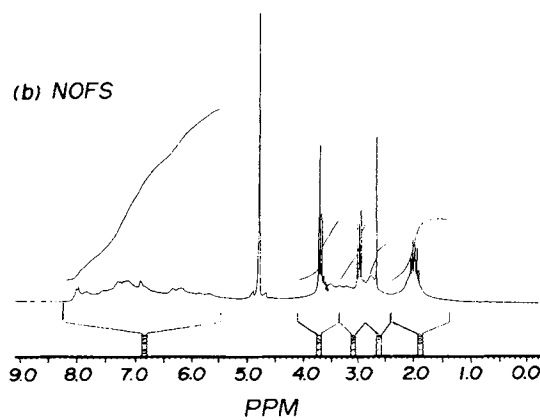
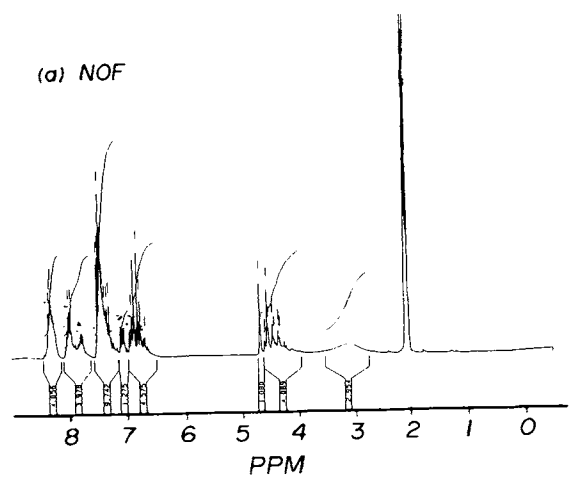


Figure 2 (a) ¹H-NMR spectra for NOF; (b) ¹H-NMR spectra for NOFS.

Table II Formulation for Dispersing C. I. Navy Blue 79 and C. I. Brown 1 Dyes in Water

Material	Weight (g) ^a	
	Navy Blue 79	Brown 1
Navy Blue 79	50	—
Brown 1	—	50
Water	6	6
Milled ball	100	100
Dispersant	21	16

^a The solids content of the wet cake was 35% for C. I. Navy Blue 79 and 45% for C. I. Brown 1.

(6 g) and mixed with the dye (C.I. Navy Blue 79, 50 g), then balls (ball no. 350, diameter 5 mm, 100 g) were added for milling. The mixture were milled mechanically by a paint shaker (Red Devil Co.) for 60 min at room temperature. All of the prepared pastes were assessed by the following methods.

Rheological Method. Ten milliliters of the dispersed paste was put in an adapter with a SCS-31 spindle, and its viscosity was measured by using a rotating cylindrical viscometer (Brookfield DVII LVT). The apparent viscosities (under a fixed shear rate) were used as a parameter to assess the dispersing ability of the prepared dispersants. All of the viscosities were measured at 25°C.

Scanning Electron Microscopy (SEM). The dispersed paste (ca. 1 g) was coated on a thin copper plate (with a wet film thickness of 12.5 μm). After drying (at room temperature for 1 day), a small piece of the paste (ca. 4 × 4 mm) was sputter-coated on an aluminum sheet (with a diameter of 20 mm) and sputter-coated with a layer of gold. The surface of the coating film was observed using an SEM electron probe microanalyzer (Hitachi F-4010).

Sedimentation. The dispersed pastes (ca. 40 mL) were put into 50 mL graduated cylinders, and the tops of the cylinders were sealed. The heights of the precipitate in the cylinder were recorded as a function of time; thus, the rate of sedimentation and the final volume ratio of the sedimentation volume to total volume were measured.

RESULTS AND DISCUSSION

Conventional NSFs were reported to be prepared by a sulfonation reaction on naphthalene at 120–160°C

followed by a condensation with formaldehyde (HCHO) at 95°C.^{7,8} In this study, separate sulfonate-grafted naphthalene formaldehyde condensates (NAFS and NOFS) were obtained by the condensation of naphthol or naphthylamine with formaldehyde followed by a ring-opening reaction with propane sultone (Scheme 1). The amino or hydroxyl group of naphthylamine or naphthol, respectively, activates the methylenation process due to the resonance effect of the amino group of naphthylamine or the hydroxyl group of naphthol; thus, the methylenation reaction is fast. Too high temperatures or too long reaction times caused gelation of the reaction system. Thus, the reaction temperature was fixed at 95°C and the reaction time was used to control the degree of condensation. The sulfonyl group of NSF was obtained by using a large amount of concentrated H₂SO₄ (98%), where H₂SO₄ also acted as a catalyst. For NOFS or NAFS, the sulfonyl group is obtained from propane sultone, not from concentrated H₂SO₄; thus, a low concentration of HCl (ca. 0.3 molar ratio of naphthol or naphthylamine) was used as catalyst instead of the concentrated H₂SO₄ to avoid the side reaction that causes sulfonation on the aromatic ring.

The grafted sulfonyl group of the title compounds (NAFS and NOFS) were obtained by the ring-opening reaction of propane sultone. The hydroxyl group on naphthol or the amino group on naphthylamine are weak bases; however, the basicity is

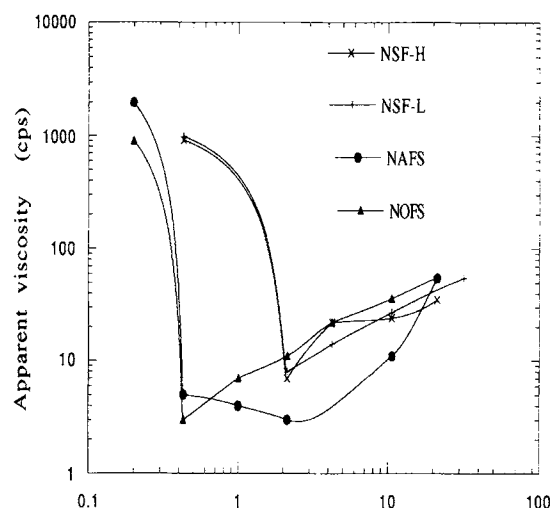


Figure 3 The apparent viscosity (cps) of the dispersed C.I. Brown 1 dye as a function of dispersant concentration (wt % based on dry dye) for NAFS, NOFS, NSF-H, and NSF-L.

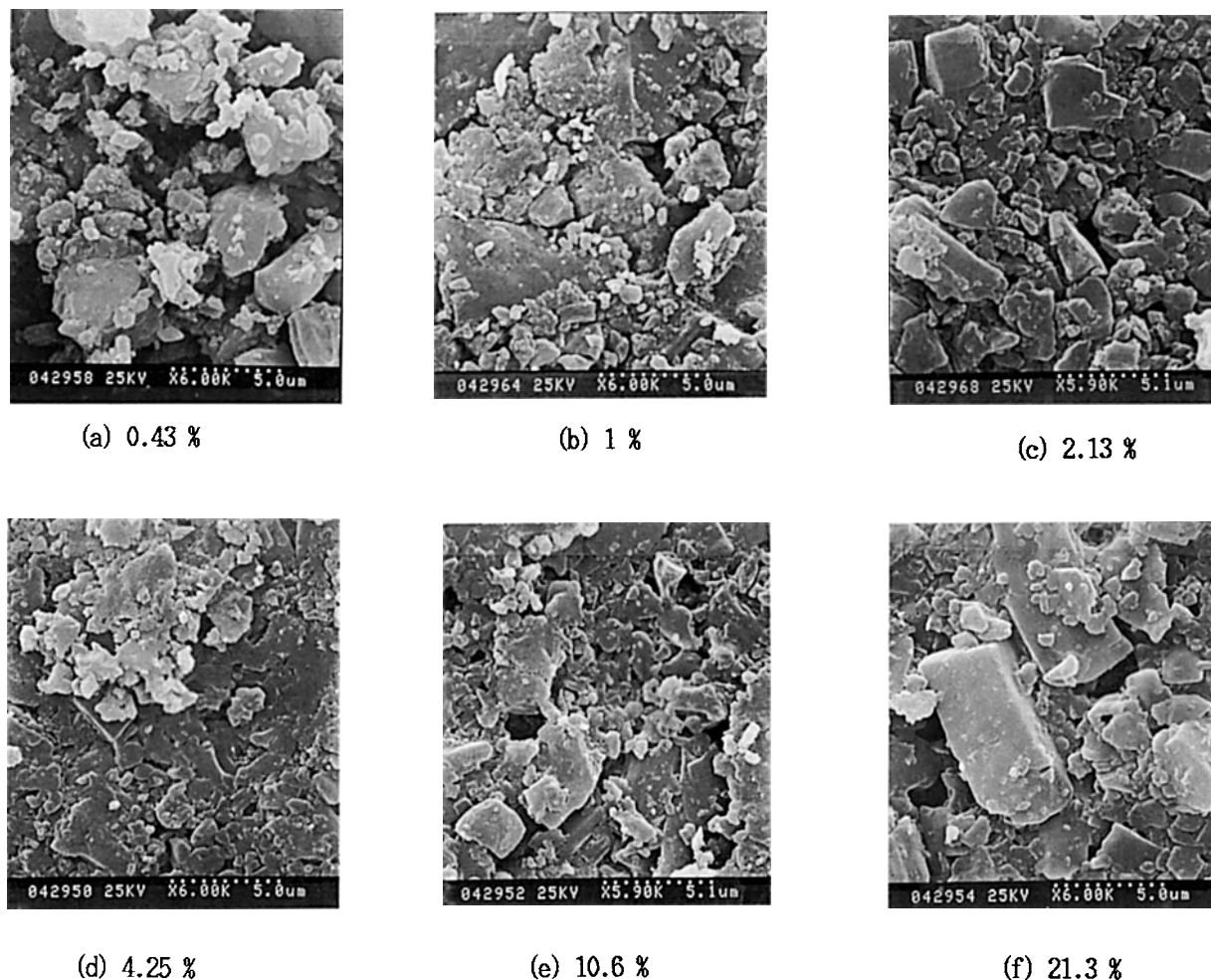


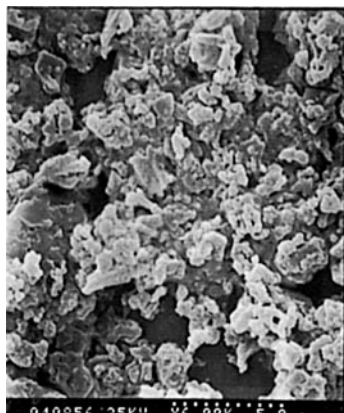
Figure 4 SEM micrography for C.I. Brown 1 dispersed in water using different concentrations of NAFS as dispersant: (a) 0.43% (b) 1%, (c) 2.13%, (d) 4.25%, (e) 10.6%, and (f) 21.3%.

strong enough to react with sultone under mild conditions, i.e., the reaction was carried out at 70–80°C without acid catalyst (see Table I).

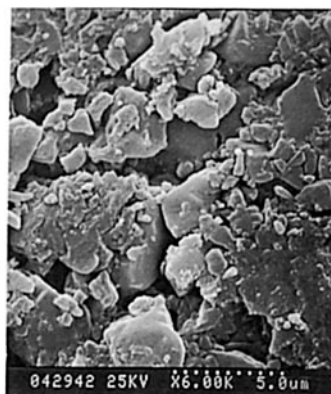
The formation of the condensates was characterized by NMR, as well as GPC. In $^1\text{H-NMR}$, both NAF and NOF have the methylene peak at $\delta = 4.0\text{--}4.5$ ppm [Figs. 1 (a) and 2 (a)] as does NSF,¹³ which cannot be observed for α -naphthol or α -naphthylamine. The appearance of several peaks at $\delta = 3.5\text{--}4.0$ ppm indicates the nonequivalence of the protons in different methylene groups, since, on the naphthalene ring, the carbon attached to the methylene group can be neighbored with a carbon either substituted by a amino group (or hydroxyl group) or not. Meanwhile, the area ratio of the methylene protons to the aromatic protons of the α -naphthylamine (α -naphthol) moiety cannot be used to ac-

curately estimate the degree of polymerization of NAFS (or NOFS) (n value of NAFS or NOFS), because the ratio does not appreciable change with the n value. The appearance of a $-\text{CH}_2-$ peak only offers evidence for the existence of the methylene group on NAFS or NOFS. After the reaction of propane sultone with NAF and NOF, the peaks at $\delta = 2.6\text{--}3.7$ ppm and $\delta = 1.7\text{--}2.2$ ppm appear both for NAFS and NOFS [Figs. 1 (b) and 2 (b)]. Because the samples prepared for NMR characterization have been purified by reprecipitating in acetone, the existence of the peak at $\delta = 2.6\text{--}3.7$ ppm and $\delta = 1.7\text{--}2.2$ ppm, which can be observed for propane sultone, indicates that the propane sultone has reacted onto the condensates.

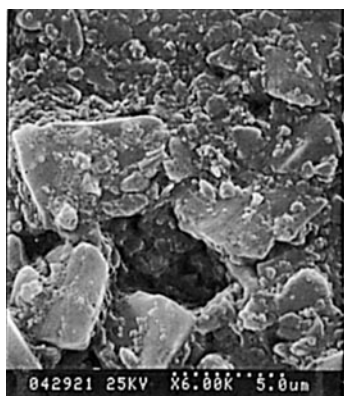
Conventional NSF is a condensate with a degree of polymerization of 2–10. Such a low-molecular-



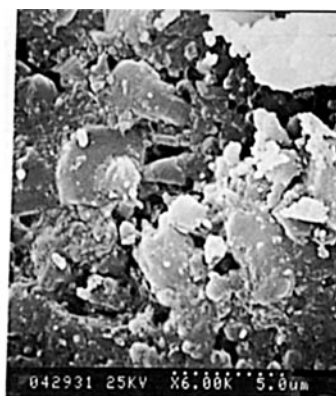
(a) NAFS



(b) NOFS



(c) NSF-H



(d) NSF-L

Figure 5 SEM micrography for C.I. Brown 1 dye dispersed in water using (a) NAFS, (b) NOFS, (c) NSF-H, and (d) NSF-L as dispersant at each optimum concentration.

weight polymer was qualitatively characterized by thin layer chromatographs⁹ or by GPC.¹⁴ For either case, the molecular weight was never calculated, but only the shape of molecular weight distribution determined GPC or the number of spots on a thin layer plate was shown. If the molecular weight of NSF is calculated using the GPC data based on a poly(ethylene oxide) calibration standard, the calculated molecular weight is tremendously high, which does not make physical sense. In the GPC spectra, there exists many peaks for both NAFS and NOFS. These peaks demonstrate that NAFS and NOFS are comprised of condensates with different degrees of polymerization.

For a dispersed system with a high solids content, the shear rate ($\dot{\gamma}$) and the shear stress (τ) have a

functional relationship of $\tau = k \dot{\gamma}^n$.^{18,19} On a plot of τ vs. $\dot{\gamma}$ for plastic flow, the intercept and the apparent viscosity ($\tau/\dot{\gamma}$) are useful parameters to monitor the extent of dispersion of a system. For a well-dispersed system, the particle aggregates are small and less associated, and the viscometer spindle senses a smaller hindrance from aggregates at a given shear rate. Consequently, a smaller shear stress and a lower viscosity were detected. In contrast, the agglomerates of a poorly dispersed system forms a network that hinders the spindle and results in a higher shear stress and a higher viscosity.²⁰

A Brookfield DVII LVT (a low shear rate viscometer), with a SCS-31 spindle was used to measure the apparent viscosity. Figure 3 shows the apparent viscosity as a function of the dispersant con-

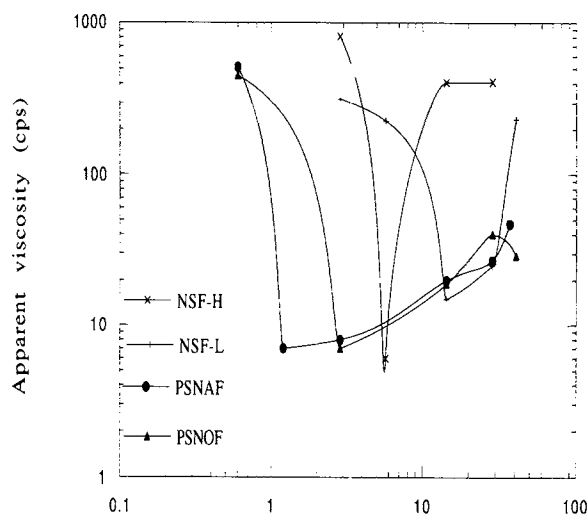


Figure 6 The apparent viscosity (cps) of the dispersed Navy Blue 79 dye as a function of dispersant concentration (wt % based on dry dye) for NAFS, NOFS, NSF-H, and NSF-L.

centration for C.I. Brown 1 dye dispersed in water using commercial high and low molecular weight NSF (NSF-H and NSF-L, respectively) as well as NAFS and NOFS as dispersants. At low concentrations of dispersant, the viscosity decreases and then slowly rises as a function of increasing dispersant concentration for each dispersant. There also exists a minimum in the apparent viscosity (called minimum viscosity) for each dispersant (NAFS, NOFS, NSF-H, and NSF-L). The minimum viscosity that NAFS or NOFS reaches is lower than that attained by NSF-H, and NSF-L. The dispersant concentration necessary to reach the minimum viscosity (called optimum concentration) is ca 0.4 wt % and 0.4–2 wt % for NOFS and NAFS, respectively, and 2% for NSF-H and NSF-L. For industrial applications, a good dispersant is expected to reach a lower minimum viscosity and to have a lower optimum concentration.

Scanning electron microscopy (SEM) can be used to observe the surface of the film prepared from the dispersed particles so that the dispersion state of the particles in solution can be assessed. The pastes of the dispersed particles were coated on metal plates for SEM observation. Figure 4 shows the SEM micrograph at a magnification of 6000 times for the paste of C.I. Brown 1 dye dispersed in water using different concentrations of NAFS dispersants. These concentrations correspond to the points shown in the plots of NAFS in Figure 3. Obviously, the particles in the paste obtained at a NAFS concentration,

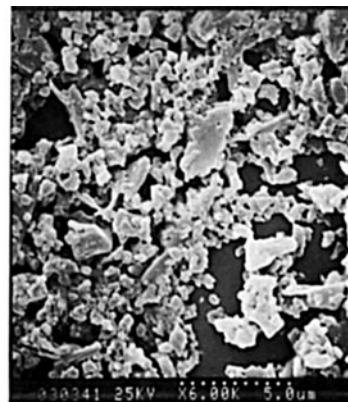
which resulted in a minimum viscosity value, are more homogeneously dispersed [see Fig. 4(c)] than those at other concentrations [see Fig. 4(a) and (b)]. Meanwhile, the pastes that exhibited the minimum viscosities in Figure 3 were also coated on metal plate so as to compare the best dispersion state for each dispersant. The results show that the pastes that reached the lower minimum viscosity (i.e., 0.43 wt % for NOFS, and 1.0 wt % for NAFS) exhibited more homogeneously dispersed particles (Fig. 5). Those results agree with our previous works,²¹ i.e., under comparable conditions, a suspension with a lower viscosity is more homogeneously dispersed.

NAFS, NOFS, NSF-H, and NSF-L were also used to disperse Navy Blue 79 dye following a given formulation (Table II). The NAFS and NOFS exhibited lower optimum concentration value in increasing order: NAFS < NOFS < NSF-H < NSF-L. For NAFS, and NOFS, the paste can reach a lower viscosity than that obtained for NSF-L (Fig. 6). The pastes that have the minimum viscosities for each dispersant in Figure 6 were coated onto metal plates for SEM analysis. Obviously, NAFS (1.2 wt %) and NOFS (1.9 wt %) exhibited the more homogeneously dispersed particles (Fig. 7) than NSF-H (5.7 wt %) and NSF-L (14.3 wt %). The above-mentioned pastes were also utilized for the sedimentation tests (Fig. 8). NAFS (1.2 wt %) and NOFS (2.9 wt %) showed the lower final residual volumes as compared to NSF-H (5.7 wt %) and NSF-L (14.3 wt %). From the results of sedimentation tests (Fig. 8) and the SEM analysis (Fig. 7), obviously, the plate exhibiting a lower final residual volume is composed of particles with smaller size. From Figures 6, 7, and 8, it could be concluded that NAFS and NOFS show better dispersing ability to Navy Blue 79 dye than NSF-H and NSF-L.

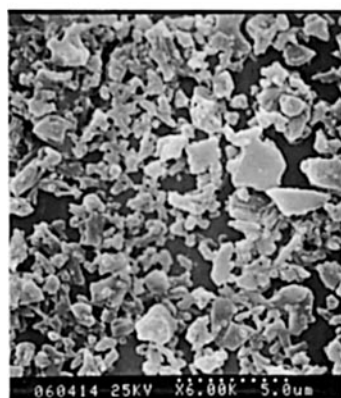
The ability of a dispersant to stabilize specific particles is related to the effective thickness ($1/\kappa$) of the adsorption layer,²¹ which in turn, is a function of the orientation of the dispersant at the adsorption layer.^{22,23} Both NAFS and NOFS have a separate grafted sulfonate group, whereas the sulfonate group of NSF is on the backbone of the condensates, i.e., there exists four carbon atoms between the aromatic ring and the sulfonate group in NAFS or NOFS; however, the sulfonate group is directly anchored onto the aromatic ring in the case of NSF. Consequently, the sulfonate group in NAFS and NOFS, which adsorb on Brown 1 or Navy Blue 79 dye particle, can be extended more fully toward the bulk phase as compared to that NSF-H or NSF-L dispersants, so that NAFS or NOFS can result in a



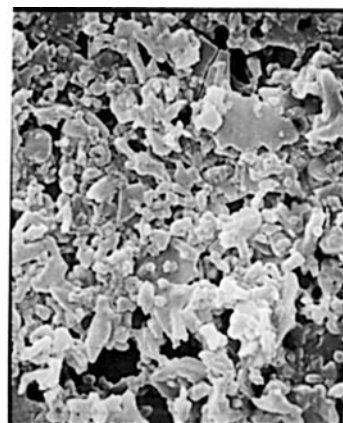
(a) NAFS



(b) NOFS



(c) NSF-H



(d) NSF-L

Figure 7 SEM micrography for C.I. Navy Blue 79 dye dispersed in water using (a) NAFS, (b) NOFS, (c) NSF-H, and (d) NSF-L as dispersant at each optimum concentration.

higher effective thickness, which is reflected by their better dispersing ability.

SUMMARY

Compared to NSF milder reaction conditions for methylenation (i.e., 95°C, 4 h), and a low concentration of HCl (ca 0.3 molar ratio of monomer) is used for synthesizing α -naphthylamine (or α -naphthol)-formaldehyde condensates. The formation of these condensates was characterized by NMR, i.e., both NAF and NOF exhibited a methylene peak at $\delta = 4.0$ – 4.5 ppm. After the reaction of NAF and NOF with propane sultone, peaks at $\delta = 2.6$ – 3.7 ppm and $\delta = 1.7$ – 2.2 ppm appear both for NAFS and NOFS,

indicating that the propylsulfonate group has been successfully introduced into the condensates.

Compared to NSF, the NAFS and NOFS show significantly lower minimum viscosities and optimum concentrations when dispersing C.I. Brown 1 dye particles. Correlating the SEM and viscosity results, it can be concluded that the suspension with a lower viscosity is more homogeneously dispersed, and also, the dispersant, which can attain the lower viscosity, has a better dispersing ability.

For Navy Blue 79 dye particle, NAFS and NOFS show significantly lower optimum concentrations and minimum viscosities. Also, these dispersants, which can attain lower viscosities compared to the commercial NSF dispersants, result in a smaller final volume fraction based on sedimentation studies.

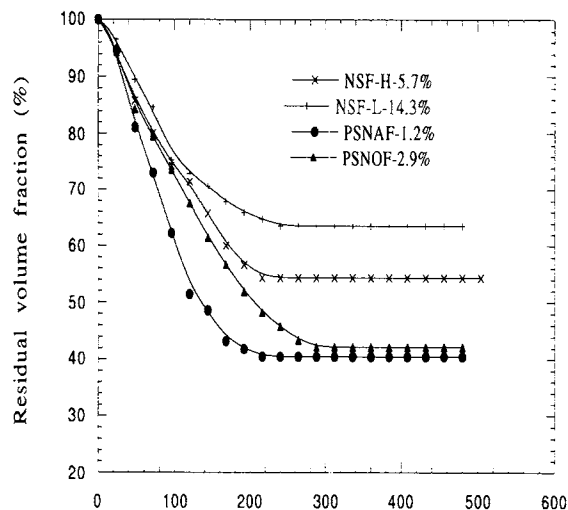


Figure 8, Time (hr)

Figure 8 The residual volume fraction of Navy Blue 79 dye dispersed in water as a function of standing time, using different dispersants (NAFS, NOFS, NSF-H, and NSF-L) at their optimum concentrations.

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REFERENCES

- G. D. Parfitt, *Dispersion of Powders in Liquids*, 3rd ed., Elsevier Applied Science Publishers, New York, 1981, p. 363, 395, 471.
- T. C. Patton, *Paint Flow and Pigment Dispersions*, 2nd ed., Wiley, New York, 1979, p. 273.
- F. P. Henry, *Organic Coating Technology*, Vol. 2, Wiley, New York, 1970, p. 675.
- P. D. Bisio, J. G. Cartledge, W. H. Keesom, and C. J. Radke, *J. Colloid Interface Sci.*, **78**, 225-234 (1980).
- C. E. Brown and D. H. Everett, *Adsorption at the Solid/Liquid Interface in Colloid Science*, D. H. Everett, Ed., Vol. 2, Chemical Society, London, 1975.
- D. H. Napper, *J. Colloid Interface Sci.*, **58**, 390 (1977).
- K. Hattori and Y. Taniko, *J. Chem. Soc. Jpn., Ind. Chem. Sect.*, **55**, 63 (1963).
- A. Pierre, J. M. Lamarche, R. Mercieer, and A. Foissy, *Chem. Congr. Res.*, **19**, 692 (1989).
- K. Hattori and Y. Tanino, *Kogyo Kagaku Zasshi*, **66**, 55 (1963).
- K. Hattori, A. Ota, and H. Madea, *J. Chem. Soc. Jpn., Ind. Chem. Sect.*, **67**, 1401 (1964).
- J. E. Funk, U.S. Pat. 88, 815 (1979).
- M. J. Rosen, *Surfactants and Interfacial Phenomena*, Wiley, New York, 1978, p. 252.
- H. A. Szymanski and A. Bluemle, *J. Polym. Sci., Part A*, **3**, 63 (1974).
- W. Dankelman and Jan de Wit, *Angew. Makromol. Chemie*, **62**, 101 (1974).
- C. J. Pouchert, *The Aldrich Library of NMR Spectra*, 2nd ed., Vol. 2, Aldrich Chemical Company, Milwaukee, WI, 1983.
- Q. T. Pham, R. P. Tiaud, M. F. Llauro, and H. Waton, *Proton and Carbon NMR Spectra of Polymers*, Wiley, New York, 1984.
- J. F. Rabek, *Experimental Methods in Polymer Chemistry*, Wiley, New York, 1980, p. 419.
- R. F. Ficher, *Ind. Eng. Chem.*, **56**(3), 41 (1964).
- Paul C. Hiemenz, *Principles of Colloid and Surface Chemistry*, Marcel Dekker, New York, 1977, p. 453.
- T. A. Strivens, *J. Colloid Interface Sci.*, **57**, 476 (1976).
- B. A. Firth and R. J. Hunter, *J. Colloid Interface Sci.*, **57**, 248 (1976).
- (a) P.-L. Kuo, J.-S. Lin, and B.-S. Wey, *J. Appl. Polym. Sci.*, **47**, 521 (1993); (b) P.-L. Kuo and B.-S. Wey, *J. Appl. Polym. Sci.*, **50**, 95 (1993).
- W. Heller and T. L. Pugh, *J. Polym. Sci.*, **67**, 203 (1960).

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