

Aqueous dispersion stability of nickel powders prepared by a chemical reduction method

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Spherical nickel powders with the very smooth surface and the uniform size of 300 nm have been manufactured by the chemical reduction and post-treatment technique. The adsorption isotherms of various water-soluble polymers on nickel powders were measured, and their effects on the dispersion stability were investigated. The adsorption amounts of polymers such as PVP (polyvinyl pyrrolidone), PMAA (polymethacrylic acid), and PAAm (polyacrylamide) on nickel powders could be successfully determined by the UV-absorbance analysis technique. Simultaneously, the dispersion stability of nickel powders in the polymer solution was evaluated in terms of the sedimentation behavior and relative coagulation rate. These results showed that the polymers such as PAAm and PVP (Mwt. 1,300,000) were found to be very effective for stabilizing the aqueous nickel dispersion system, and consequently, the coagulation rate of nickel powders in the PAAm solution was almost 100 times slower than that in pure water. © 2004 Kluwer Academic Publishers

1. Introduction

Current trends towards miniaturization and operation at higher frequencies of electronic devices require that electronic components be of a small size, have high volumetric efficiency, a high reliability with compact chip configurations, which is cost effective [1]. Based on advanced tape-casting, screen-printing and surface mounting technologies, multilayer monolithic ceramic devices are promising candidates to meet these requirements. In case of multilayer ceramic capacitors (MLCC), miniaturization is progressing steadily as 1005 → 0603 → 0402 (0.4 mm × 0.2 mm).

Keeping up with the trend in miniaturization of electronic components, the demand for MLCC has rapidly grown because of the large capacitance despite its small size. The capacitance can be enhanced through thinning dielectric and electrode layers as well as increasing the number of layers. In recent years, MLCCs that use the internal electrodes made from Ni pastes have been successfully developed to meet the growing need for low cost capacitors [2]. However, Ni powders composing the pastes for fabricating thin electrode layers should be spherical nano particles with narrow particle size distribution. Although the primary particles of Ni powders manufactured by the chemical reduction method are very small, these powders are easily agglomerate

due to the quantum size and the magnetic property. In this study, the surface modification technique of Ni powders in order to prevent agglomeration has been investigated. In particular, we focused on the adsorption behaviors of various water-soluble polymers on Ni powders and the dispersion stability in an aqueous system.

2. Experiment and method

2.1. Materials

2.1.1. Polymer

PVP (polyvinyl pyrrolidone, Mwt. 1,300,000) and PMAA-Na (Poly (methacrylic acid, sodium salt), Mw 9,500 Mn 5,400) were provided by Aldrich Chemical Corporation. PAAm (Acrylamide, polymer 10% solution, Mwt. 300,000) was obtained by Wako Chemical Corporation, Japan. A known weight of each polymer was mixed and stirred in appropriate weights of DI water to obtain the 2 wt% stock polymer solution.

2.1.2. Powders

Ni powders were obtained from Changsung Co. Ltd., South Korea as shown in Fig. 1. The powders obtained for this study were used to synthesize the chemical

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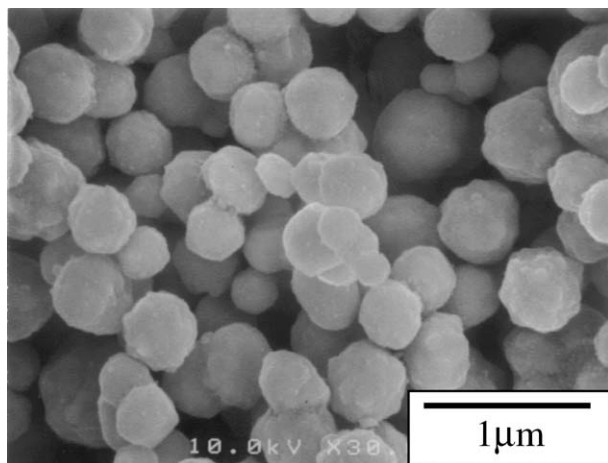


Figure 1 SEM micrograph of nickel powders used in this work.

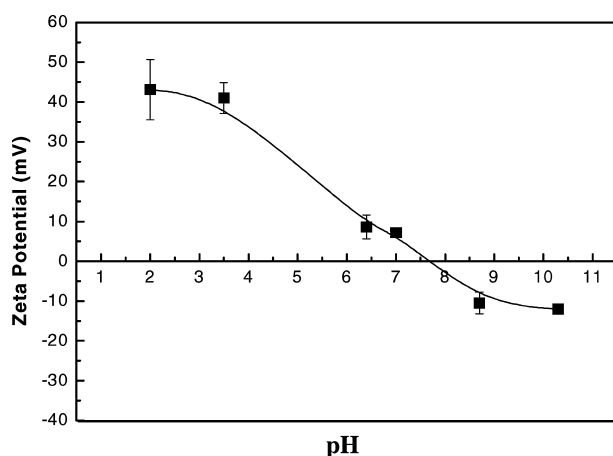


Figure 2 Zeta-potential of nickel powders as a function of pH.

reduction method along with nickel nitrate and hydrazine in an aqueous solution. Pulverization and heat treatment in a N_2 atmosphere of nickel powders were carried out as post-treatments. The specific surface area of these powders was found to be $2.24 \text{ m}^2\text{g}^{-1}$ using BET surface area analyzer (Gemini 2375, Micromeritics, USA). The primary particle size of nickel was found to be 300 nm as determined by the scanning electron microscope (SEM, Model S4200, Hitachi, Tokyo, Japan). The iso-electric point of nickel powders, determined by zeta potential analyzer (ZetaPlus—Particle Size Analyzer, Brookhaven Instruments Co., USA), was about pH 8 shown in Fig. 2.

2.2. Experiment

2.2.1. Adsorption isotherms

The overall experimental flow chart for this study on measuring adsorption amounts of various polymers is given in Fig. 3, and the detailed experimental procedure in each step is stated below.

Samples for adsorption experiments and stability analysis were prepared at a volume of 30 ml contained in 50 ml screw capped glass bottles. Polymer solutions of a known concentration of each polymer were prepared in water. Nickel powders (0.7 g) were equilibrated with polymer solutions (30 mL) of different concentrations for more than 20 h at 30°C . After equilibrium

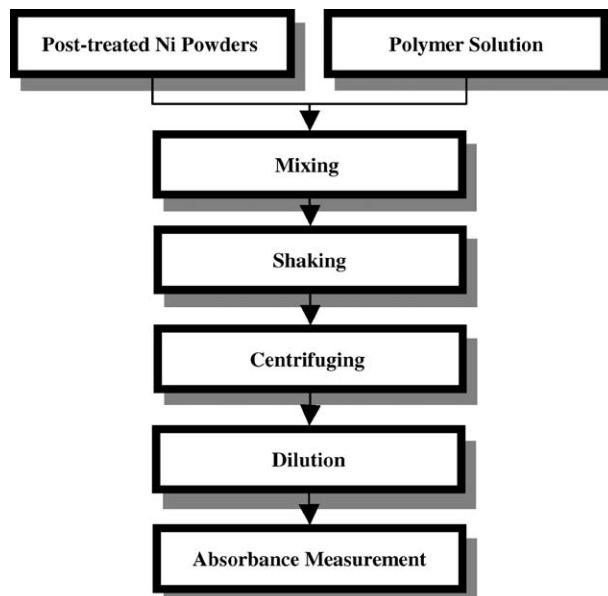


Figure 3 Overall experimental flow chart.

was reached, the supernatant liquid was separated by centrifugation, and its absorbance was measured on a UV/VIS/NIR Spectrometer (V-570, Jasco, Japan) using 1 cm path length cells. Calibration curves were used for quantitative estimation of polymers. The supernatant was then analyzed for the polymer concentration and the adsorbed amount was calculated from the difference between the initial concentration and the final concentration in the supernatant.

2.2.2. Dispersion stability

The stability of each Ni suspension to the presence of added polymer was determined by a method similar to the turbidity method. The stability of the suspensions was inferred from optical transmittance measurements as a function of time using a UV/VIS/NIR Spectrometer (V-570, Jasco, Japan) at 500 nm. Transmittance data was recorded at 10 s intervals during 600 s. An increase of transmittance due to the settling of the particles shows the sedimentation behavior of powder in the suspension.

3. Results and discussion

3.1. Adsorption isotherms

The polymers adsorbed on the surfaces of the metal particles can control particle size and prevent agglomeration. This stabilizing action by an adsorbed nonionic polymer layer is generally referred to as steric stabilization. In aqueous media, sterically stabilized aqueous systems are usually much less sensitive to added electrolyte than electrostatically stabilized systems. In addition, there are three advantages of steric stabilization: (1) equal efficacy in both aqueous and non aqueous dispersion media, (2) equal efficacy at both high and low solids content, (3) reversibility of flocculation [3].

The specific adsorption of the various polymers onto the particle surface in water is illustrated in Fig. 4. The adsorption isotherms appear to follow the Langmuir-typed behavior, suggesting that a monolayer coating of

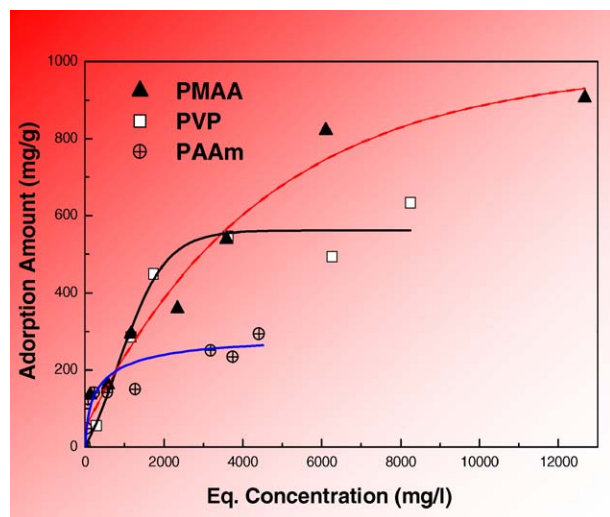


Figure 4 Adsorption isotherms of different polymers on nickel powders at 30.

the polymer molecules has been formed on the particle surface. In all cases, the amount adsorbed increases as the polymer concentration increases, until a plateau is reached. The maximum adsorbed amounts of PAAm, PVP, and PMAA on Ni powders at 30°C are 270, 540, and 900 mg/g, respectively. The slope, before the adsorption isotherm reached the plateau, is considered an indication of the adsorption affinity of the polymers to the surface and can be used to predict the suspension stability [4]. Fig. 4 shows the adsorption affinity of the polymers to the surface is expressed in a reducing order of PAAm > PVP > PMAA, and the dispersion stability of polymer-Ni systems follows the same order (Figs 5b, 6b, and 7b). This suggests that the suspension stability and the sedimentation behavior are closely related to the adsorption characteristics of the polymers in an aqueous system.

In the case of PVP, the steric effect arising from the long polyvinyl chains of PVP on the surface of nickel particles may contribute to the anti-agglomeration. Because the steric effect is largely determined by the covered fraction of PVP on the surface of the nickel particles, it was, therefore, necessary that there be enough PVP to adsorb on the nickel particles. It could be explained that the stabilization by PVP adsorption in the aqueous solution is due to the steric stabilization caused by the entropic interaction between the long protruded tails of the adsorbed PVP polymers. In this study, it may be considered that the dispersion stability is the highest when the amount adsorbed on Ni powders is about 540 mg/g.

PMAA-Na used in this study is an anionic polyelectrolyte. The dissociation reaction of PMAA-Na creates free carboxylic acid groups that can be neutral COOH or dissociated to COO⁻. Depending on the solvent conditions, pH and ionic strength, the fraction of functional groups dissociated (COO⁻) and non-dissociated (COOH) will vary. The fraction of dissociated groups increases with increasing pH from acidic pH to basic pH. As the degree of dissociation increases, the polymer charge varies from relatively neutral to highly negative [5]. It is concluded that the adsorbed amount of

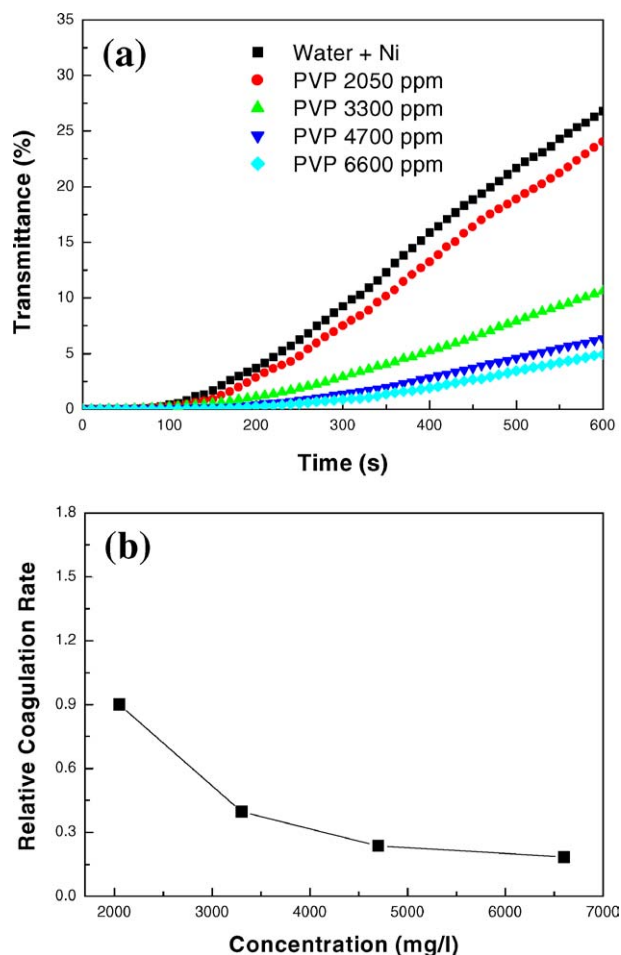


Figure 5 Variations of (a) transmittance of Ni-PVP suspensions at 500 nm with time and (b) RCR value of Ni-PVP suspensions with concentration of PVP.

PMAA on Ni particles is very sensitive to pH variations. In this study, COO⁻ groups existed more than the COOH groups because adsorption experiments were conducted in the range of pH 7–8. It is suggested that the adsorbed amount of PMAA on Ni powders is higher than other polymers because the negatively charged functional groups dissociated (COO⁻) easily adsorb onto the Ni surface, which is to charged nearly zero (see Fig. 3) at the range of pH 7–8.

In the case of PAAm, the adsorption isotherm shows a steep increase at lower concentrations, and thereafter attains saturation coverage. This isotherm exhibits high affinity behavior resulting in good dispersion stability although the adsorbed amount is smaller than other polymers. Chibowski *et al.* showed that the influence of pH about adsorption amounts of PAAm on particles is noticeably small. That is because two types of functional groups exist in its macromolecule —NH₂ and —COOH, which may turn into NH₃⁺ and —COO⁻ in different pH of solutions. Existence of these groups in PAAm macromolecule causes adsorption of PAAm on the oxide surface which is less sensitive to the changes of the pH of the solution [6]. Moreover, a lower number of —COOH groups in the PAAm chains, in comparison to PMAA chains, is probably the reason for the fact that the adsorbed amount of PAAm on Ni particles is much lower than that of PMAA.

3.2. Dispersion stability

Coagulation rate (a) is often expressed in relative terms as the so-called stability ratio, W . This ratio is defined as

$$W = k(f)/k \propto 1/a \quad (1)$$

where the slow coagulation rate, k is the number of collisions that result in coagulation, and the rapid coagulation rate, $k(f)$ can either be a theoretical value or the number of collision between particles [7]. In the fast regime, $W \approx 1$, whereas in the slow regime $W \gg 1$. But the reliable methods for routine measurement of suspension stability by steric effect are lacking although the coagulation rate experiments for the measurement of suspension stability have been performed. So, we redefined the stability ratio (W_s) in the dispersion system by the steric effect in this study because we had difficulty in evaluating dispersion stability with using W .

W_s (stability ratio)

$$\begin{aligned} &= \frac{\text{Transmittance of aqueous dispersion system without dispersant after 600 s}}{\text{Transmittance of aqueous dispersion system with dispersant after 600 s}} \\ &= \frac{1}{\text{RCR}} \end{aligned} \quad (2)$$

As described in the experimental procedure, the transmittance of suspensions was measured using a vis-

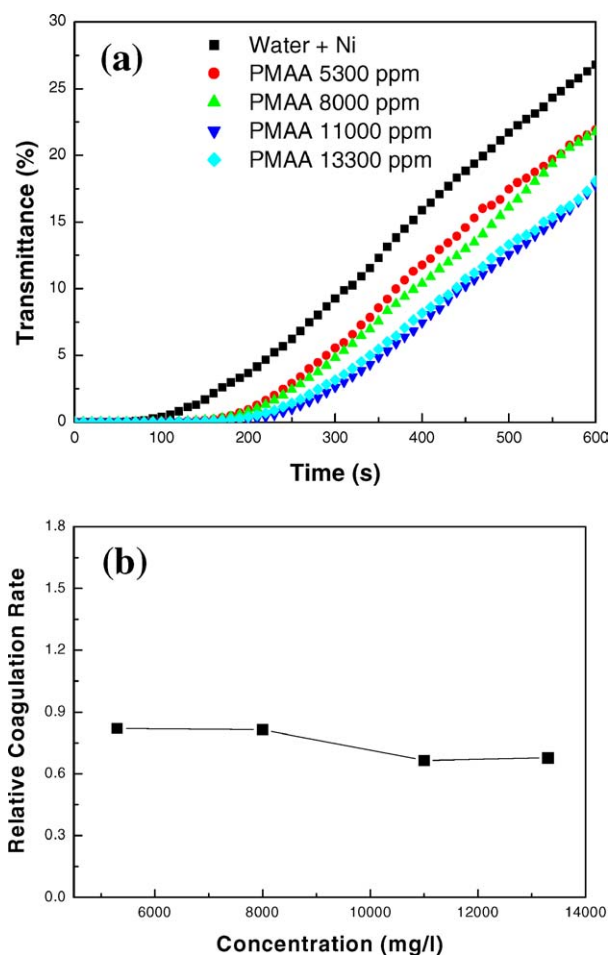


Figure 6 Variations of (a) transmittance of Ni-PMAA suspensions at 500 nm with time and (b) RCR value of Ni-PMAA suspensions with concentration of PMAA.

ible light of 500 nm. Coagulation ratio is inversely proportional to stability ratio at the steric dispersion as shown (1). As a result, we could define $1/W_s$ as RCR (Relative Coagulation Rate) as described (2) and evaluate dispersion stability of different suspensions using RCR value. Low values of RCR indicate that particles are stable (i.e., coagulate at a slow rate), while high values of RCR are indicative of unstable suspensions.

The influence of PVP on the stability of Ni particles according to PVP concentration is shown in Fig. 5, in terms of relative coagulation rate, RCR. The results demonstrate that the RCR value of PVP-Ni suspension becomes small with increasing concentrations of PVP until the RCR value of 0.18 at 6700 ppm, that is, the dispersion stability is gradually increased. But, in the range of more than 4700 ppm, the difference of RCR values decreases slightly with increasing concentration. The dispersion stability of Ni powders reaches the maximum when long chains of PVP completely covered the surface of the Ni particles at the range of about 4700 ppm. Although dispersion stability of the suspension increases a bit at the range of more than 4700 ppm, it was generated not by the dispersion behavior through the steric effect of PVP adsorption on Ni particles but by the viscosity of the polymer solution.

As can be seen in Fig. 6, RCR values of PMAA-Ni suspensions decrease a little according to the increasing of the PMAA concentration (RCR value is almost

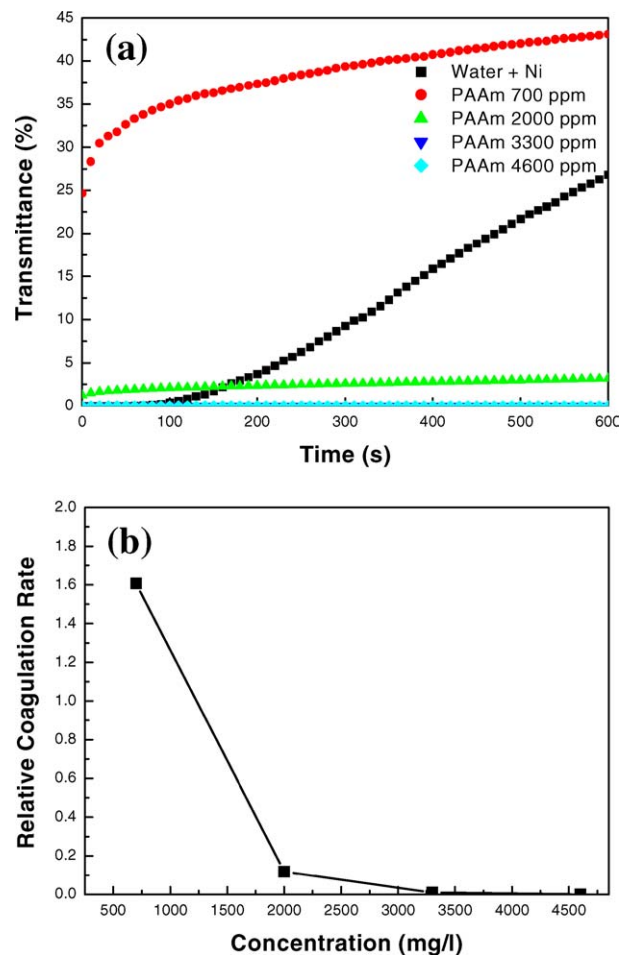


Figure 7 Variations of (a) transmittance of Ni-PAAm suspensions at 500 nm with time and (b) RCR value of Ni-PAAm suspensions with concentration of PAAm.

0.8–0.7). It is shown that the coagulation of particles rapidly goes on though the adsorption amounts of PMAA on Ni powders are higher than other polymers. Shih *et al.* showed that the PMAA chains become uncharged and the formation of loops in the adsorbed configurations is, in principle, enhanced at the acidic pH range due to a lower fraction dissociated. Therefore, it is suggested that for pH 7–8, a large fraction of PMAA chains dissociated and a negatively charged sites on the polyelectrolyte chains non-attached tend to repel each other; and this repulsion preferably forces particles to agglomerate.

Fig. 7 depicts the dispersion stability of Ni suspension stabilized by PAAM as a function of PAAM concentration. The RCR value recorded the minimum of 0.01 at 4600 ppm, that is, the highest dispersion stability of suspension that is noticeably obtained. At the concentration of more than 2000 ppm, the dispersion stability of suspension could be maintained. At the lower concentration of PAAM (<700 ppm), PAAM did not completely adsorb onto the surface of the Ni particles and form a bridge between them causing agglomeration. In addition, unless the reaction time of adsorption was sustained sufficiently, the Ni particles were agglomerated at more than the adsorption saturated concentration. But Ni powders in the PAAM solution obtained high dispersion stability at the concentrations of more than 3300 ppm and maintained the disper-

sion stability for 3 h after adsorption reaction reached equilibrium.

Fig. 8 exhibits vials of the nickel powder dispersions in the different PAAM concentrations. As shown in Fig. 8b, the vials containing concentration of greater than 2500 ppm show good dispersion stability after 3 h. It is demonstrated that the coagulation rate of nickel powders in the PAAM solutions was almost 100 times slower than that in pure water.

4. Conclusions

The adsorption isotherms of polymers such as PMAA (polymethacrylic acid), PVP (polyvinyl pyrrolidone), and PAAM (polyacrylamide) on nickel powders could be successfully determined by the UV-absorbance analysis technique. The adsorption isotherms appeared to follow the Langmuir-typed behavior and the maximum amounts adsorbed of PAAM, PVP, and PMAA on Ni powders at 30°C were 270, 540, and 900 mg/g, respectively. The adsorption affinity of the polymers to the surface was expressed in a reducing order of PAAM > PVP > PMAA and the dispersion stability of polymer-Ni systems followed the same order. This suggested that the dispersion stability and the sedimentation behavior were closely related to the steric effects caused by the adsorption characteristics of polymers in the aqueous system.

The dispersion stability of Ni-polymer suspensions could be effectively evaluated in terms of the transmittance and the RCR (relative coagulation rate) value of suspensions. The polymers such as PAAM and PVP (Mwt. 1,300,000) were highly effective for stabilizing the aqueous nickel dispersion system, and consequently, the coagulation rate of nickel powders in the PAAM solution was almost 100 times slower than that in pure water. The dispersion stability of suspensions was not much improved even after adding more than the saturated amount of adsorption of each polymer.

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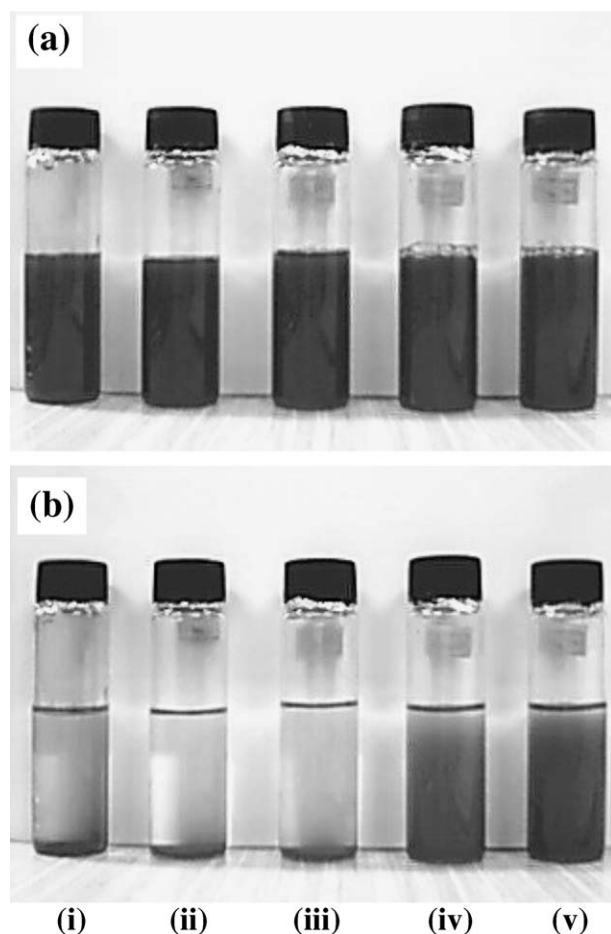


Figure 8 Photographs of vials (50 ml) containing Ni powders dispersed in the aqueous solutions with (i) no addition, (ii) 65, (iii) 650, (iv) 2500, and (v) 4000 ppm of PAAM: (a) at initial and (b) after 3 h.

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