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Rinsing effect of alkaline electrolyzed water on nickel surfaces

TOSHIKAZU TAKENOUCHI* and SHIN-ICHI WAKABAYASHI
Shiko electric industries Co., Ltd, 36 Kita-Owaribe, Nagano-shi, Nagano, 3810–014, Japan
*(*author for correspondence, fax: + 81-26-263-4562, e-mail: ttakenoh@shinko.co.jp)*

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Abstract

The improvement in the surface cleanliness of electroplated nickel by rinsing in alkaline electrolyzed water (AEW) was determined. When the nickel plated sample was rinsed with the AEW, it was found that the amount of residual sulfate ion on the surface of a sample decreased approximately by half compared to one rinsed only with de-ionized pure water. Because nanosize hydrogen bubbles are present in the AEW, and the zeta-potential has a negative value, we then surmised that the mechanism of rinsing was as follows: The sulfate ions are selectively absorbed on the nanosize colloidal hydrogen bubbles, or substituted for anions absorbed on the hydrogen bubbles. The sulfate ions absorbed on the nickel surface then become detached. The detached sulfate ions are absorbed on the surface of the hydrogen bubbles, and negatively charge the hydrogen bubbles. It can be considered that any detached sulfate ions do not re-adhere due to the electrical repulsion force of the negatively charged nickel surface. Thus the sample is efficiently rinsed.

1. Introduction

The solution in the cathode compartment obtained by the electrolysis of a dilute electrolyte solution, i.e., alkaline electrolyzed water (AEW), has a negative, low reduction/oxidation potential, as well as alkalinity. We have already reported that AEW is useful for removing grease and washing electronic parts that contain copper [1]. Furthermore, we have reported that carbon steel immersed in AEW of a sodium carbonate solution became resistant to corrosion [2]. Therefore, we have tried to rinse plated samples on which ionic contamination remains without causing any corrosion using AEW.

In general, because a plating bath contains a significant amount of electrically conductive salts and metal salts, ionic contamination is liable to remain on the surface of electroplated electronic parts. Therefore, various methods, for example, washing many times with pure water, using warm water, and adopting ultrasonic cleaning, have been generally devised in order to eliminate ionic contamination from the cleaning process after plating. In the Watts bath, in which nickel sulfate is the main component, it is known that the surface cleanliness of the nickel plated product is poor because sulfate ions are liable to remain on its surface. Moreover, as for silicon wafers washed with a sulfuric acid/hydrogen peroxide mixed solution, it is reported that the complete removal of the sulfate ions is very difficult even if it is then rinsed with pure water [3, 4]. As described above it is known that the sulfate ions are not totally removed by rinsing though the mechanism is not clear.

In this study an attempt was made to improve the surface cleanliness of nickel plated samples by rinsing with AEW, which was effective for the cleaning of electronic parts, and eliminating the sulfate ions, which were only slightly removed by conventional cleaning with pure water. Furthermore, the zeta-potential of the AEW used for rinsing was measured, as was the particle size distribution of the hydrogen bubbles in the AEW, and then the rinsing effect mechanism was developed.

2. Experimental

2.1. *Reagent, sample, and apparatus*

The electrolyte used for producing the electrolyzed water, sodium nitrate, sodium chloride, calcium chloride dihydrate, sodium nitrate, sodium carbonate decahydrate, ammonium chloride, ammonium sulfate, ammonium nitrate, ammonium acetate, or ammonium carbonate (all analytical reagent grade chemicals by Wako Pure Chemical Industries, Ltd.) was used. Each chemical was dissolved in pure de-ionized water to prepare the respective 0.1 M aqueous solutions. As a further step these aqueous solutions were electrolyzed and AEW was then prepared. A diaphragm-type electrolytic device (MIZ, Ltd., JED-007) was used for manufacturing AEW. This apparatus consisted of anode and cathode compartments and a diaphragm, which separated the compartments. Titanium electrodes coated with a platinum layer were used. The dimensions of both electrodes were 74 × 113 mm. The electrolysis was carried out at 0.72 A dm^{-2} (0.6 A, 100 V) for 15 min. The pH and redox potential (ORP: oxidation reduction potential) of the solution were measured using a pH meter (Horiba, Ltd., F-22) and an ORP meter (Toko Science Laboratory, TRX-90), respectively. The concentration of the nickel ions eluted in AEW was measured by ICP (Inductively Coupled Plasma spectrometer, Japan Jarrel Ash, Model 575 mark II). A 20 × 20 × 1 mm oxygen-free copper plate was used as the sample for the plating. Semi-gloss electrolytic nickel plating with a thickness of 1 μm was applied. The composition of the nickel-plating bath was 250 g l^{-1} of sodium sulfate, 40 g l^{-1} of nickel chloride, 40 g l^{-1} of boric acid, and 2 g l^{-1} of sodium saccharate. The plating condition was 2 A dm^{-2}, for 5 min at 45 °C. The ionic impurities on the surface of the sample were quantitatively determined using a liquid ion chromatograph (DIONEX, Model DX120) based on JIS (Japanese Industrial Standards) K0556. The particle size distribution of the hydrogen bubbles was measured using a Microtrack particle size distribution analyzer (Nikkiso, UPA-EX). The zeta-potential was determined using a zeta-potential analyzer (Brookhaven Instruments Corp., PALS Zeta potential analyzer). Pure water with a 16 Ω cm or higher resistivity was used.

2.2. *Rinse*

Before starting the experiments, the pH and redox potential of AEW used for the various electrolytes shown in section 2.1 were determined in order to select the best water for rinsing. Two kinds of electrolytes were selected based on these results.

The samples were treated using the following steps.

1. The copper plate specimen was nickel plated by electro-deposition in the nickel plating bath.
2. The nickel plated specimen was bound with a polyester thread and suspended; then it was soaked in 0.5 l of AEW. The sample was repeatedly soaked and pulled out three times. The total soaking time was 3 seconds (hereafter, this operation is termed AEW rinse).
3. The specimen was washed for one minute in a stream of pure water flowing at 2 l min^{-1}.
4. The specimen was dried using hot air.
5. The specimen was boiled in the ultra-pure water, and the concentrations of the anions and cations present in the boiled water were determined by ion chromatography.
6. The amount of the ionic impurities on the sample per unit area was obtained. In order to compare the rinse efficiency of AEW to that of the other cleaning liquids, similar operations were carried out using sodium hydroxide aqueous solution of pH 12 and pure water instead of AEW. Moreover, in order to determine the dissolution of nickel, the rinsed sample was soaked for one month, and the dissolution was determined. Figure 1 shows the set-up and procedure.

2.3. *Particle size distribution and zeta-potential*

The particle size distribution of the hydrogen bubbles present in AEW was determined by light scattering photometry using a quartz cell. The zeta-potential was measured at 25 °C and an applied voltage of 2.5 V using a quartz cell.

3. Results and discussion

3.1. *Characteristics of various AEW*

Immediately after electrolysis, the pH and redox potential of each AEW were measured. These results are shown in Figure 2. The relation between the pH and the hydrogen generating potential is expressed by $E_H = -RT/2F \ln P_{H_2} - 0.059\text{pH}$ vs. NHE ($E_H = -0.059\text{pH}$ at 25 °C, 1 atm). It was confirmed that the measured pH-potential values of all AEWs coincided with this equation. Hydrogen and sodium hydroxide

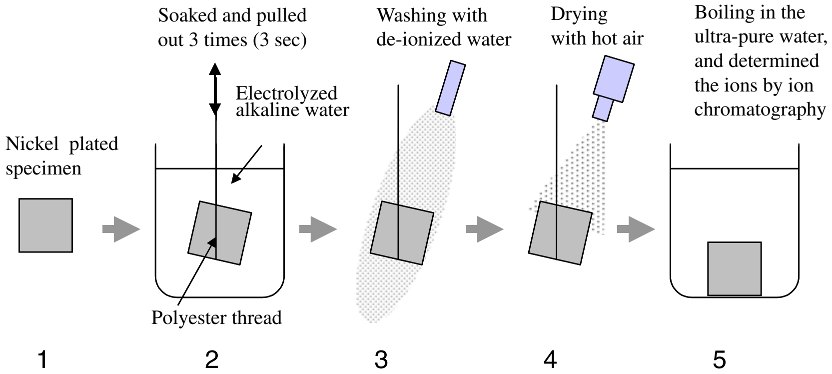

Fig. 1. Rinsing procedure and setup.

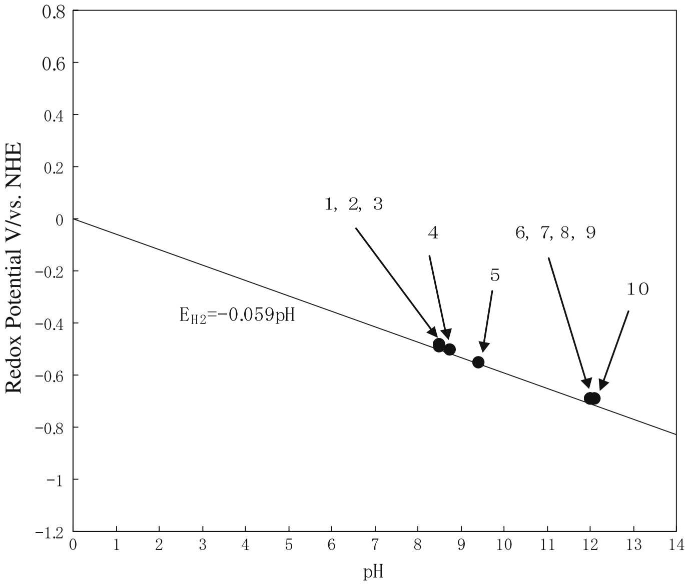

Fig. 2. Potential–pH diagram for electrolyzed alkaline water. 1: Ammonium chloride, 2: Ammonium sulfate, 3: Ammonium nitrate, 4: Ammonium carbonate, 5: Ammonium acetate, 6: Sodium chloride, 7: Sodium carbonate decahydrate, 8: Sodium nitrate, 9: Sodium sulfate, 10: Calcium chloride dihydrate. All electrolytes concentration is 0.1 M.

were formed at the cathode. According to the Nernst equation, the higher the pH and the more negative the redox potential, the greater the hydrogen partial pressure of AEW. Though the concentration of the dissolved hydrogen was not determined in this experiment, Kikuchi showed that molecular hydrogen is dissolved in the solution when its concentration is below 0.75 mM and exists as bubbles when it is greater than 0.75 mM [5]. Because it was considered that these hydrogen bubbles might improve the rinse effect as described later, the electrolyzed water for rinsing was prepared using sodium chloride and sodium carbonate decahydrate, and adjusted to a pH of 12 and a redox potential of −0.69 V vs. NHE. We did not use the nitrate because it required waste water treatment.

3.2. *Amount of ionic impurities on samples*

The amount of ionic impurities remaining on the surface of the sample is shown in Figure 3. The experiments were carried out three times and their average value is indicated. The lower limit of determination for the chloride ion, sulfate ion, and sodium ion using an ion chromatograph was 0.05, 0.1, and 0.02 μg l^{-1}, respectively.

The amount of the sulfate ion remaining on the sample surface was 122×10^{-9} g cm^{-2}, or 120 $\times 10^{-9}$ g cm^{-2}, respectively, when the rinsing was done with pure water or sodium hydroxide aqueous solution of pH 12. When the rinsing was done by AEW prepared from sodium carbonate, and from sodium chloride, both values were 40×10^{-9} g cm^{-2}. When the rinsing was done with the de-ionized water, the sulfate ion tended to remain on the surface of the sample. On the other hand, when the rinsing was done with AEW the amount of the sulfate ion decreased and the efficacy of rinsing was confirmed. No difference was observed in any of the cases for the chloride ion and their values were lower than that of the sulfate ion. In other words the chloride ion can be easily removed compared to the sulfate ion. The effect of removing the cation with AEW is uncertain because the amount of sodium ions, which was considered to originate from the electrolyte, was low even before the rinsing.

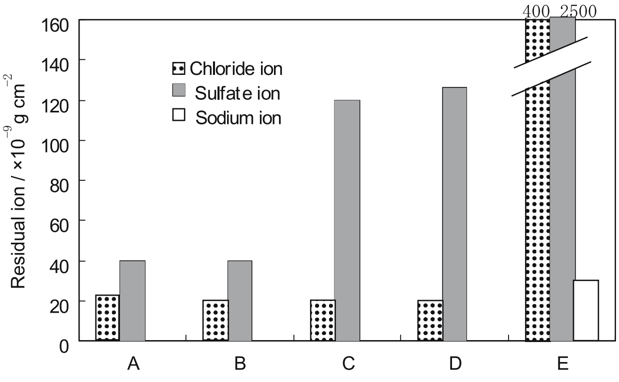

Fig. 3. After rinsing ionic contamination on electroplated nickel specimen. Rinsed by A: NaCl alkaline electrolyzed water, B: Na_2CO_3 alkaline electrolyzed water, C: NaOH solution, D: de-ionized water, E: As plated without rinse.

3.3. *Dissolution of nickel*

Nickel dissolution was not detected in any of AEWs. This is attributable to the fact that nickel lies in the passivation area of the Pourbaix diagram [6] because the AEW had a pH of 12 and a redox potential of −0.69 V vs. NHE. The pH and redox potential of the electrolyzed water are important parameters when rinsing metal parts.

3.4. *Hydrogen bubbles existing in AEW*

It was found that the peak in the distribution of the hydrogen bubble diameter was around 1–2 μm, and that nanosize hydrogen bubbles were immediately formed after electrolysis. The nanosize bubbles changed to micron size bubbles having a diameter from 2 to 5 μm with time. Furthermore, the size of all the bubbles converged in the range from 0.01 to 0.03 μm 1 h later. It is considered that these big bubbles were formed by combining the nanosize bubbles, and the nanosize bubbles not combined disappear gradually. These results are shown in Figure 4. When the hydrogen content in the aqueous solution exceeds its solubility, it has been determined that two kinds of hydrogen, i.e., dissolved hydrogen in the form of molecules in the water and colloidal microbubbles, are present [5]. Moreover, there are many reports about the size and behavior of the hydrogen bubbles cathodically. It has been reported that hydrogen microbubbles almost disappear within 1–6 h though it depends on the electrolysis conditions [7].

3.5. *Zeta-potential*

The zeta-potential of AEW was -28 mV after electrolysis and increased with time. On the other hand, the zeta-potential of the sodium hydroxide solution, which had the same pH as that of AEW, was 0 mV, and did not change with time. These results are shown in Figure 5. The fact that the zeta-potential of AEW exhibited a large negative value indicates that the hydrogen produced by electrolysis exists as a nanosize colloid and is negatively charged. Moreover, it is considered that the hydroxide ions are being adsorbed on the surface of these hydrogen bubbles [8]. Consequently, sulfate ions are considered to be adsorbed by hydrogen bubbles and removed during the rinse process with the AEW. The decrease in the zeta-potential is attributable to fadeout of the hydrogen bubbles.

3.6. *Mechanism*

The cathode water, obtained by the electrolysis of the ultrapure water, or ultra-pure water, in which hydrogen is dissolved, has a rinse effect and removes the nonionic particulates on the surface of silicon wafers. These solutions are now being used for cleaning silicon wafers [9]. The mechanism of this cleaning process is considered to be as follows: Hydrogen bubbles in aqueous solution adhere to the particulates and lift them off the silicon wafer [10]. The Surface of silicon wafer and particulates have large negative zeta-potential; therefore the removed particulates and silicon wafer do not re-adhere to each other due to electrical repulsion forces [11]. In addition, the microbubbles obtained by stirring air into the water is reported to have the effect of removing dirt that adheres to the substrate [12]. Moreover, it is reported that the microbubbles have a high negative zeta-potential [13]. Thus, the microbubbles and the zeta-potential have a close relationship with the particulate removal mechanism.

In this study, it has been confirmed that sulfate ions adhering to the surface of plated nickel could be efficiently rinsed off using AEW. Moreover, no efficacy was observed for AEW in which the hydrogen bubbles disappeared one week after preparation. Based on these results it can be considered that these hydrogen bubbles play a key role in removing sulfate ions. It was confirmed that AEW used in this experiment contained nanosize hydrogen bubbles, and that these have a negative zeta-potential of -28 mV immediately after electrolysis. Based on this, the mechanism of desorption of the sulfate ions adsorbing on the surface of nickel can be considered to be that the sulfate ions are selectively adsorbed by the nanosized colloidal hydrogen bubbles, or that the sulfate ions are substituted for the anions which are adsorbed by the hydrogen bubbles. Moreover, as in the case of the particulate removal mechanism on a silicon wafer, it is proposed that removed sulfate ions do not re-adhere because of the electrical repulsion force with the negatively charged nickel surface.

3.7. *Advantage of rinsing with AEW*

Water with dissolved hydrogen gas also has a rinsing effect. The shortcomings of the hydrogen gas solution include the following: (1) hydrogen gas supply and safety equipment are required; (2) it cannot control the pH without acid or base; and (3) the amount of hydrogen dissolved in the hydrogen gas solution is less than that of the electrolyzed solution. In contrast, the advantages of AEW include the following: (1) with only an electrolytic device, pure water and electrolytes electrolyzed water can be supplied anywhere, any time; (2) AEW can control the pH level and the redox potential of the solution and, even for some highly corrosive metals, AEW can even prepare the solution in the stability region based on the Pourbaix diagram; and (3) AEW can contain a super-saturated amount of dissolved hydrogen [5]. It is likely that AEW has a higher rinsing effect than solution with dissolved hydrogen gas. This is an issue yet to be clarified.

Furthermore, expensive apparatus is required to produce cathode water by electrolyzing ultra-pure water or to prepare ultra-pure water in which hydrogen is dissolved. However, the equipment to electrolyze dilute electrolyte and make AEW for industrial applications can be purchased at a price several times less than the above mentioned equipment (approximately 6–10 million yen).

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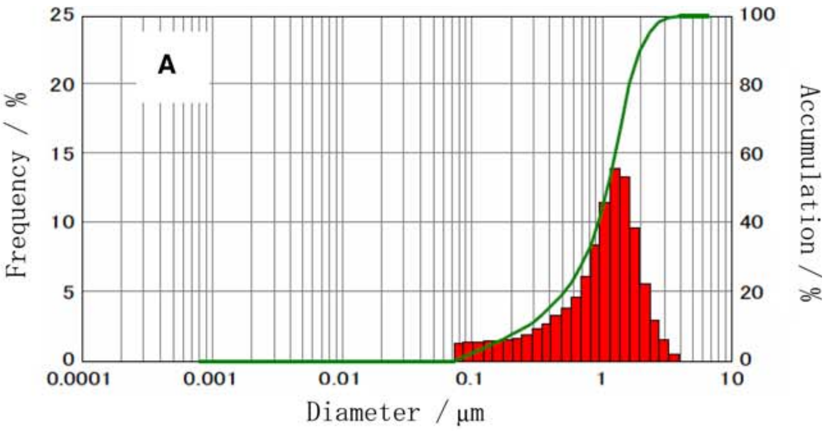
Fig. 4. Distribution of hydrogen bubble sizes in the alkaline electrolyzed water. Measured after electrolysis, A: 0 h, B: 15 min, C: 30 min, D: 60 min.


A
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15
10
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Accumulation / %
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80
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1
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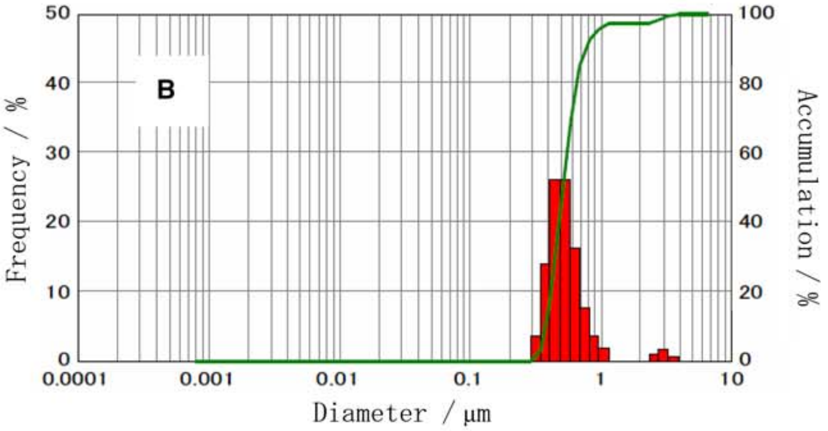
Diameter / μm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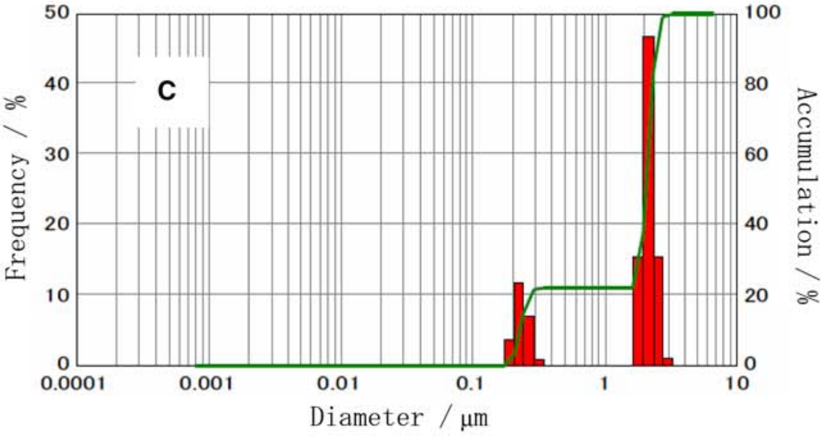
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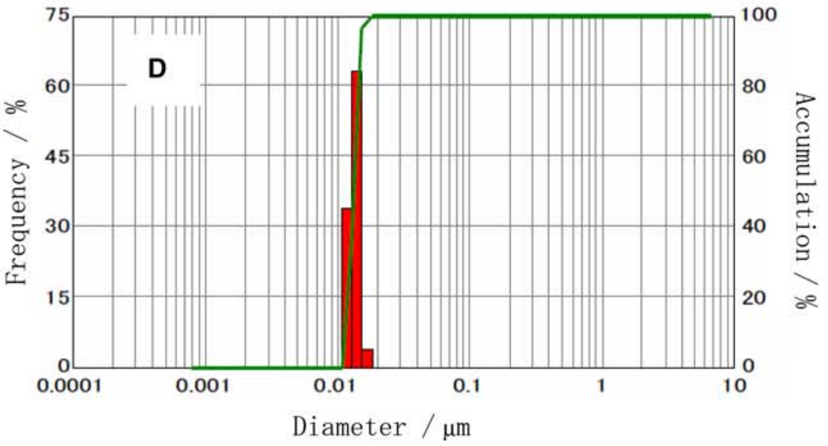
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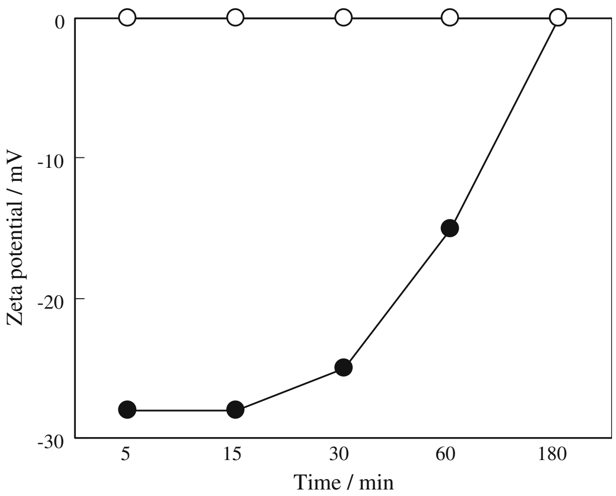

Fig. 5 Zeta potential •: NaCl alkaline electrolyzed water, ○: NaOH solution.

4. Conclusion

Improvement of the surface cleanliness of an electro-nickel plated sample was investigated by rinsing the sample with AEW. The amount of sulfate ions remaining on the sample surface significantly decreased when it was rinsed with AEW after plating compared to a sample rinsed only with pure water. Because nanosize through submicron sized hydrogen bubbles exist in AEW, and the zeta-potential of AEW has a high negative value compared to that of alkaline aqueous solution of pH 12, the mechanism of removal of sulfate ions using AEW can be postulated as follows: The sulfate ions are selectivity adsorbed by the nanosize colloidal hydrogen bubbles present in AEW, or the sulfate ions adsorbed on the surface of the nickel are desorbed by substituting for the anions which are being adsorbed on the hydrogen bubbles. Moreover, removed sulfate ions do not re-adhere because of the electrical repulsion force with the negatively charged nickel surface.

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