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Synthesis and Application of Hydrogenated Cardanol Polyoxyethylene Ether

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Abstract. Unsaturated cashew phenol polyoxyethylene ether (UCPE-11, UCPE-13) was synthesized from cashew phenol by ethylene oxide addition reaction, and then hydrogenation was catalyzed at room temperature and pressure to produce saturated cashew phenol polyoxyethylene ether nonionic surfactants (CPE-11, CPE-13). The effects of catalyst dosage and reaction time on catalytic hydrogenation reaction were investigated. The optimum conditions for catalytic hydrogenation reaction were determined as follows: Al-Ni alloy was selected as catalyst at 25 °C, the dosage of which was 18% and 27.8% of the mass of unsaturated cashew phenol polyoxyethylene ether, respectively, and the reaction time was 11 h and 12 h. The structure of the product was characterized by IR and ^{1}H NMR. The synthetic product was used in AC aluminium cleaner. The results show that the product has excellent decontamination performance. The surface of the washed aluminum parts is clean and has a metallic luster, and the washing effect is good.

1. Introduction

Chemical cleaning of metal parts processing in mechanical industry is to clean the surface of all kinds of metal parts, profiles before and after processing, metal surface before and after processing, and before sealing and rust prevention. The cleaning object is metal surface, and the cleaning dirt is mainly metal processing including residual lubricant or equipment after cutting and forming, and rust-proof oil for sealing workpiece. The purpose of cleaning is to remove the dirt on the metal surface in the prescribed time and process conditions, without damaging the metal surface, and to meet the requirements of the next process such as electroplating, painting, assembly, etc. [1] At present, the commonly used metal cleaning agents was solvent-based, semi-solvent-based and water-based. Among them, water-based metal cleaning agents have been widely used because of their low production cost and good environmental protection performance. [2] Most of the existing water-based metal cleaning agents are surfactants composed of alkylphenol polyoxyethylene ether (OP-10), nonylphenol polyoxyethylene ether (TX-10) and Sodium Alkylbenzene Sulfonate (LAS) [3-5]. Nonylphenol polyoxyethylene ether (TX-10) is mainly used in textile, petroleum, chemical, rubber, machinery, leather and other industries. Due to the biodegradation problems, it has been banned for use in detergents. Therefore, a non-toxic and harmless ideal substitute for TX-10 is needed. Cashew nut phenol is a kind of biological resource derived from cashew nut shell liquid. It is a cheap, renewable and environmentally friendly raw material [6]. However, the application of cashew nut phenol is limited to a few industries such as coatings. The main reasons are as follows: cashew nut phenol side chain is a mixture of 1-3 unsaturated olefins, which is more active, unsuitable for storage and difficult to control reaction; Pentadecyl phenol, which is a side chain hydrogenation product, has low reaction activity; therefore, the substitution and condensation of cashew nut phenol and its

hydrogenation products, and the addition reaction technology are difficult to break through, which restricts its industrialization process [7]. In this paper, unsaturated polyoxyethylene cardanol ether was synthesized by addition reaction of cashew nut phenol with ethylene oxide. The side chain of unsaturated polyoxyethylene cardanol ether was catalyzed by hydrogenation reaction to prepare saturated polyoxyethylene cardanol ether. The cleaning effect of the synthesized product was tested in alumina pickling agent.

2. Experimental

2.1. Instruments and reagents
810FT-IR infrared spectrometer (Perkin-Elmer Corporation); AVANCE-600 NMR spectrometer (Bruker, Switzerland); 800D low-speed desktop centrifuge (Jiang Su Zhengji Instrument Co., Ltd.).

Cardanol (99.5% grade, Guangdong standard Lee Cashew Co., Ltd.); Ethylene oxide (99% grade, Wan Tianjin Chemical Materials Co.); Hydrogen (high-purity 99.9%, Xinhua Shenyang reagent factory); nickel-aluminum alloy (Sinopharm chemical reagent Co., Ltd.); sodium hydroxide (Mao Tianjin chemical reagent Factory); Absolute ethanol (Mao Tianjin chemical reagent Factory) were analytical grade; Fatty alcohol polyoxyethylene ether, nonyl phenol polyethylene polyoxyethylene ethers are permanent Shenyang Jie washing of raw materials Co., Ltd, sulfuric acid (Shenyang Chemical Reagent Factory); machining oil (Shenyang East invasive mechanical equipment Co., Ltd.).

2.2. Polyoxyethylene hydrogenated cardanol synthesis of ethylene
Unsaturated cardanol polyoxyethylene ether (UCPE-11, UCPE-13) was prepared by batch ethoxylation (direct oxidation) of 500 g cardanol in an autoclave at 135-140 °C and 2×10^5-3×10^5 Pa. Weighing 15 g Al-Ni alloy in 250 mL beaker, adding 200 mL deionized water and stirring with glass rod. The nickel catalyst for the reaction of cashew phenol polyoxyethylene ether was prepared by taking 30 g of NaOH from the balance and maintaining the temperature between 60°C and 70°C. 18 g of cardanol polyoxyethylene ether was weighed in a 250 mL round bottom flask, and then 80 g of absolute ethanol and metallic nickel were placed, and catalytic hydrogenation was carried out at 25 °C to obtain hydrogenated cardanol polyoxyethylene ether (CPE-11, CPE-13). The reaction formulas are as follows:
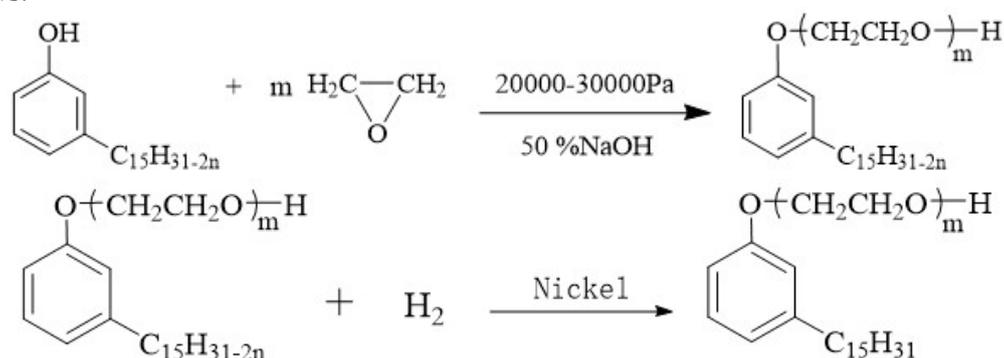
Where m =11,13；n=0, 1, 2, 3.

2.3. Nuclear magnetic resonance and infrared spectroscopy detectable product
Nuclear magnetic resonance spectroscopy: AVANCE-600 nuclear magnetic resonance spectrometer of Bruker Company in Switzerland was tested. The solvent was deuterium chloroform ($CDCl_3$).

Infrared spectrum: The blank sample used for Infrared Determination of cashew nut phenol polyoxyethylene ether product was potassium bromide tablet. After testing blank, the infrared test was carried out by dot method after saturating cashew nut phenol polyoxyethylene ether on potassium bromide tablet.

2.4. Determination of hydrophilic-lipophilic balance (HLB)

2.4.1. Determination of HLB value of synthetic saturated cardanol polyoxyethylene ether.
The HLB values of nonionic surfactants CPE-11/CPE-13 were estimated by numerical representation [8].

The HLB value of nonionic surfactants is:

$$\text{HLB value of nonionic surfactants} = \frac{\text{Hydrophilic moiety moie mass}}{\text{Surfactant molar mass}} \times \frac{100}{5}$$

The HLB of mixing two surfactants is as follows:

$$\text{HLB}_{\text{mixed}} = \frac{\text{HLB}_A \bullet \omega_A + \text{HLB}_B \bullet \omega_B}{\omega_A + \omega_B}$$

2.4.2. Determination of the optimum ratio of emulsifier required for oil pollution.
A series of emulsifiers with different HLB values are prepared by mixing CPE-11 and CPE-13 in different proportions. The mechanical processing oil was put into the emulsifier mixture of HGF-11 and HGF-13.5% of the emulsifier was added to the emulsifier, then 80% of the water was added to the emulsifier. Finally, the oil was put into the high-speed disperser at a speed of 3000 r/min and dispersed for 1 minute. After standing for 12 h and 24 h, observe and compare their stability. The best stability was the mixture ratio of HGF-10 and HGF-15.

2.5. Method for preparing aluminum acid lotion

2.5.1. Formula composition.

Table 1. Formulation of AC aluminum pickling agent

Ingredient	Proportion (%)	Quality (g)
Mixture of UCPE-11 and UCPE-13	0.804	0.804
AEO-7	0.036	0.036
AEO-9	0.36	0.36
Industrial concentrated sulfuric acid H2SO4	2	2
Deionized water	96.8	96.8

2.5.2. Preparation process.
- Accurately weigh 0.804 g of CPE in a beaker.
- Weigh 0.036 g of AEO-7 and 0.36 g of AEO-9 in the above beaker, add 46.8 g of deionized water to dissolve and stir.
- Weigh 50 g of deionized water in another beaker, slowly drip 2 g of concentrated sulfuric acid into the beaker with a burette, and stir while stirring.
- Stirring was continued for 3 min until the solution was completely transparent and cooled to room temperature to obtain an AC aluminum cleaning agent.

2.6. Cleaning ability test
Cleaning rate detection uses the differential method [9].

The aluminum sample was washed, dried and weighed, which recorded as m. The sample was immersed in machine oil, soaked for 24 hours and taken out. Dried naturally for 72 hours, weighed it, and marked it as m′.

Six beakers with 50 mL aluminium pickling agent were added to the beaker under (25+3) ℃ condition. The oil stained aluminium parts were immersed in the beaker and oscillated about 30 times. After standing for 20 minutes, they were taken out and washed with deionized water, dried and weighed, then respectively recorded as m″. Use the following formula to calculate the cleaning rate.

$$\text{Cleaning rate}(\%) = \frac{m' - m''}{m' - m}$$

Three aluminium specimens are tested in parallel, and the average value is taken as the result of the measurement. The error between each group of data and the average value should not exceed 3%. Otherwise the experiment should be re-conducted [10].

3. Results and discussion

3.1. Calculation of catalytic hydrogenation yield
In the second step of catalytic hydrogenation of the products UCPE-11 and UCPE-13 synthesized in the first step, the effects of catalyst dosage and reaction time on the reaction process were investigated, and the results were judged by the conversion rates.

According to the product data provided by the manufacturer, the proportion of each component in cashew nut phenol used in the synthesis of CPE-11 was saturated hydrocarbon: monoolefin: diene: triolefin = 5.4:48.8:16.4:29.3, and the total volume of hydrogen consumed in the reaction was 0.9645L. When CPE-13 was synthesized, the proportion of each component in cashew nut phenol was: saturated hydrocarbon: monoolefin: diene: triolefin = 5.4:48.6:16.8:29.1, and the total volume of hydrogen consumed by the reaction was 0.9646 L.

In the catalytic hydrogenation of cardanol unsaturated ether, the conversion of hydrogenation is calculated as follows:

$$\text{Hydrogenation yield} = \frac{\text{Actual consumption of hydrogen}}{\text{Theoretical consumption of hydrogen}} \times 100\%$$

3.2. Effect of Catalyst Dosage on Reaction
Under the conditions of 18g of UCPE-11 and UCPE-13, 2.5 g, 5 g, 7.5 g, 10 g, 12.5 g of catalyst were added respectively, and the time when the reaction reached equilibrium was recorded. The effect of catalyst dosage on the reflection time was investigated. See Figure 1:
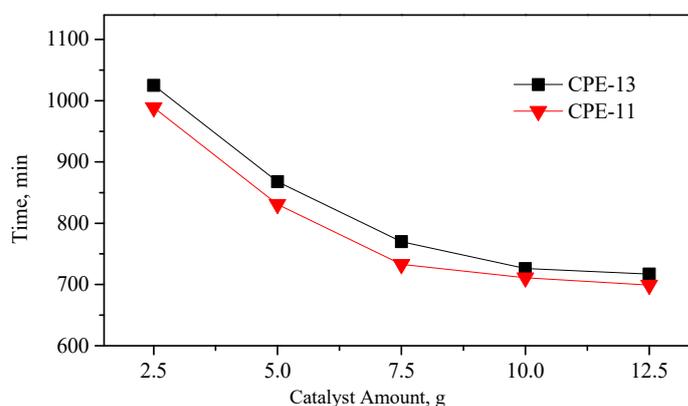
Figure 1. Effect of Catalyst on response time

As shown in figure 1, the reaction time decreased rapidly with the increase of catalyst dosage. However, when the amount of catalyst reached 7.5 g, the time required for catalytic hydrogenation of UCPE-11 did not decrease significantly with the increase of the amount of catalyst added; when the amount of catalyst reached 10 g, the reaction time remained basically unchanged. In the consideration of the cost savings, the amount of Al-Ni alloy used in this experiment was finally determined to be 7.5 g. Because the content of nickel in the catalyst was 50%, the amount of nickel catalyst used was 3.5 g, that is, the amount of catalyst used was 19.5% of the total mass. When the amount of catalyst reached 10 g, the time spent on catalytic hydrogenation reaction of UCPE-13 remained basically unchanged. In the consideration of the savings of experimental cost, the amount of Al-Ni alloy used in catalytic

hydrogenation experiment was determined to be 10 g. Because the content of nickel in catalyst was 50%, the amount of nickel catalyst used was 5 g, that is, the amount of catalyst used was 27.8% of the total mass.

3.3. Effect of reaction time on reaction

The amount of hydrogen reduction in the gas cylinder measured in this experiment is the amount of hydrogen actually consumed by the catalytic hydrogenation reaction. When the liquid level in the gas cylinder does not change within 5 h, it indicates that the reaction has reached equilibrium. The conversion rate of the catalytic hydrogenation reaction is not constant, but changes continuously with the reaction time. Therefore, determining the optimal reaction time required for catalytic hydrogenation is of great significance for reproducibility experiments and amplification experiments.

When the reactants UCPE-11 and UCPE-13 were 18 g and the amount of catalyst Al-Ni alloy was 7.5 g and 10 g respectively, the hydrogen consumption was recorded every 1 h after the start of the reaction, and the conversion of catalytic hydrogenation was calculated. The effect of reaction time on conversion was investigated. The results are shown in figure 2.
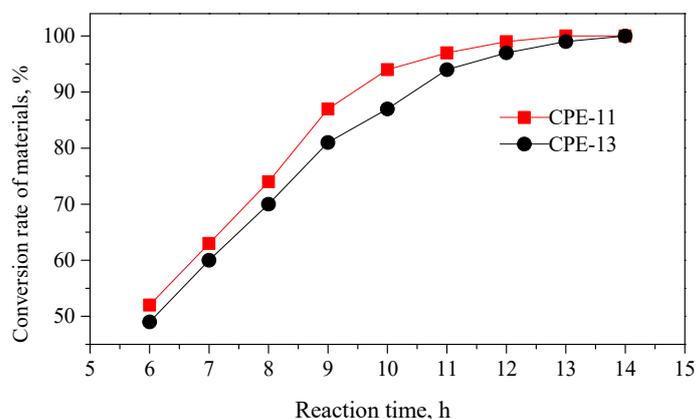
Figure 2. The effect of reaction time on conversion rate

Figure 2 showed that the conversion of UCPE-11 reached 97% at 11 h, 99% and 100% at 12 h and 13 h, but in the consideration of the cost and time factors, the optimum reaction time for catalytic hydrogenation of UCPE-11 was determined to be 11 h. The conversion of UCPE-13 reached 97% at 12 h, 99% at 13 h and 100% at 14 h, so the optimum reaction time for this catalytic hydrogenation reaction was 12 h.

3.4. Optimum conditions for catalytic hydrogenation

According to the above data, the optimum conditions for catalytic hydrogenation of UCPE-11 were as follows: using Al-Ni alloy as catalyst, the amount of UCPE-11 was 18% of the mass of UCPE-11, dissolving UCPE-11 in anhydrous ethanol and reacting for 11 hours. Under such conditions, the hydrogenation effect was ideal. The optimum conditions for hydrogenation of UCPE-13 were: using Al-Ni alloy as catalyst, 27.8% of the mass of UCPE-13, dissolving UCPE-13 in anhydrous ethanol for 12 hours. Under such conditions, the hydrogenation effect was ideal.

3.5. Structural characterization of CPE-13 and CPE-11

3.5.1. Infrared Spectroscopy.

Figure 3 is an infrared spectrum of the reaction raw materials and reaction products.
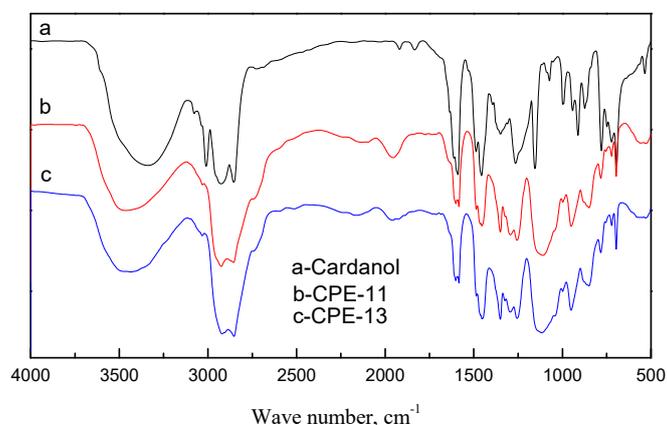
Figure 3. Infrared spectrum of reaction raw materials and hydrogenated cardanol polyoxyethylene ether

Figure 3 shows that the characteristic absorption peaks of 1643 cm^{-1} (C=C) had been weakened on the infrared spectra of CPE-11 and CPE-13, indicating that the unsaturated structure had been completely hydrogenated. Meanwhile, in CPE-11 and CPE-13, the characteristic peaks of C-O-C were found at 1255 cm^{-1}, 1116cm^{-1}, 1254 cm^{-1} and 1105 cm^{-1}, respectively, indicating that a certain number of ethylene oxide long chains were added to phenolic hydroxyl groups and a lot of alkoxy groups were added to the original structure.

3.5.2. *Nuclear Magnetic Resonance Spectroscopy (^1H NMR).*
Figure 4 is a ^{1}H NMR spectrum of the starting material cardanol.
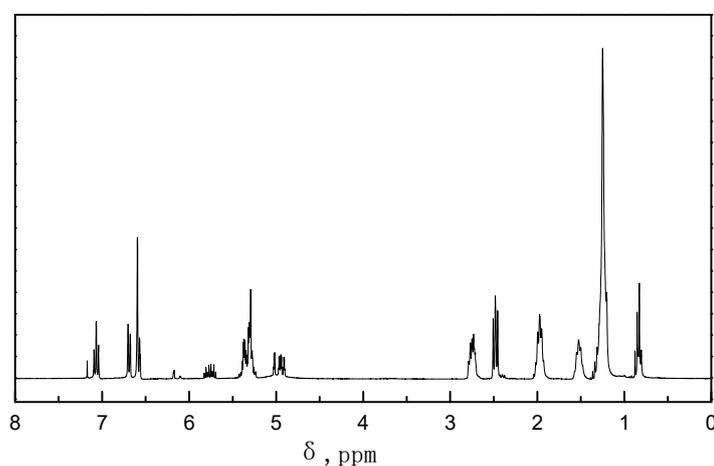
Figure 4. ^{1}H NMR spectrum of cardanol

Figure 5 is a ^{1}H NMR spectrum of the synthesized product CPE-11.
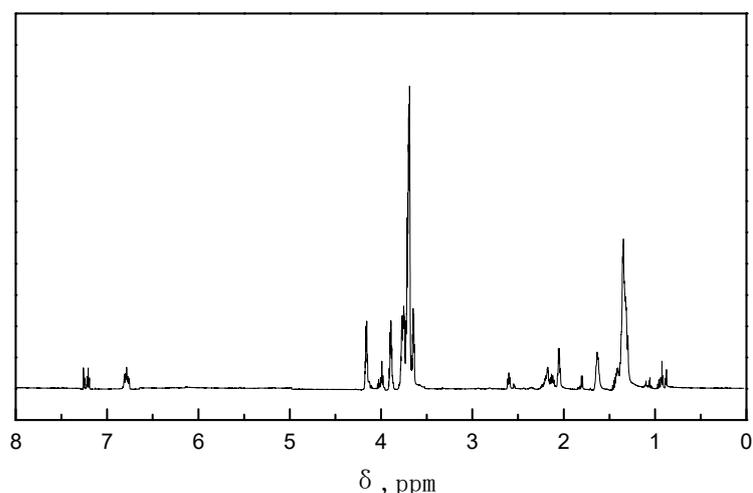
Figure 5. ^{1}H NMR spectrum of CPE-11

Figure 6 is a ^{1}H NMR spectrum of the synthesized product CPE-13.
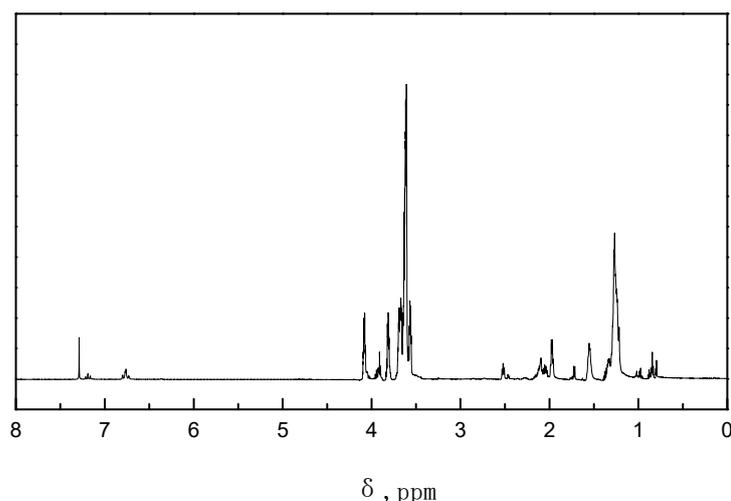
Figure 6. ^{1}H NMR spectrum of CPE-13

From figure 5 and figure 6, it could be seen that the absorption peaks of H belonging to C=C bond at the sites of cardanol δ=4.91-5.00, 5.35-5.54 and 5.71-5.84 had completely disappeared. As can be seen from figure 5, an absorption peak of a polyoxyethylene ether methylene group appeared in the vicinity of δ = 3.51-3.78, 3.84-3.87 and 4.11-4.15. From figure 6, we could see that the absorption peaks of polyoxyethylene ether methylene appeared near the values of δ=3.46-3.73, 3.76-3.79 and 4.06-4.10.

In summary, it could be concluded that the active groups of the raw material had participated in the reaction, and the reaction was complete, and the target product was produced.

3.6. Determination of HLB value

3.6.1. Determination of HLB values of CPE-11 and CPE-13.
According to the formula, the HLB values of CPE-11 and CPE-13 are approximately calculated. The results are shown in table 2.

Table 2. HLB of CPE-11and CPE-13

Product name	HLB value
CPE- 11	12.7
CPE- 13	13.2

Table 2 shows that the HLB value of CPE-13 is higher than that of CPE-11. The hydrophilicity of the product increases with the increase of ethyl oxide addition number, so the HLB value increases gradually.

3.6.2. Determination of HLB in Metal Processing Oil.
The optimum ratio of CPE-11 to CPE-13 (hereinafter referred to as CPE-13) was obtained by mixing CPE-11 and CPE-13 in 85%:15%, 75%:25%, 65%:35%, 55%:45% and 45%:55% proportions. The emulsification effect was shown in figure 7. From the comparison of figure 7, it could be seen that when the ratio of HGF-11: HGF-13 was 45%:55%, the solution emulsification effect was the best, and the HLB value of CPE was 12.97. It shows that the HLB value of CPE is similar to that of machine oil, and the HLB value of machine oil is about 12.97

Figure 7. Emulsification Effect

3.7. Determination of cleaning ability of aluminum cleaning agent
The cleaning effect of AC aluminum cleaner was measured and compared with that of the original cleaning agent used in the factory. The results are shown in table 3. As can be seen from table 3, AC aluminum cleaner has better cleaning ability and good rust resistance.

Table 3. Cleaning effect of Al cleaning agent

	AC aluminum cleaning agent	Factory original cleaning agent
Cleaning rate /%	97.6%	93.4%
Rust prevention	No rust	Partial rust

4. Conclusions
Unsaturated cardanol polyoxyethylene ether UCPE-11 and UCPE-13 are prepared from cardanol by reaction with ethylene oxide at 136-140 °C and pressure of 2×10^5-3×10^5 Pa. The saturated products CPE-11 and CPE-13 are obtained by hydrogenation of the product with nickel as catalyst. The effects of catalyst dosage and reaction time on catalytic hydrogenation reaction are investigated. The optimum

conditions for catalytic hydrogenation reaction are determined as follows: Al-Ni alloy is selected as catalyst at 25 °C, the dosage of which is 18% and 27.8% of the mass of unsaturated cashew phenol polyoxyethylene ether, respectively, and the reaction time is 11 h and 12 h.

The synthetic products CPE-11 and CPE-13 are mixed into CPE at the ratio of 45%:55%. The aluminium cleaner AC is prepared with CPE and used in aluminium surface cleaning. The results show that the cleaned aluminium surface is clean and metallic luster, and the cleaning effect is good.

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