



# The Effect of Keruing Oleoresin on the Corrosion Rate of Copper in Car Radiator Parts

Hery Tristijanto <sup>1</sup>, Iman Mujiarto <sup>1</sup>, Suyanto <sup>1</sup>, Edy Budiarmo <sup>2</sup>, Andrian Fernandes <sup>2</sup> and Arif Wahyudianto <sup>1,\*</sup>

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<sup>1</sup> 1 Mechanical Engineering Department, Politeknik Negeri Semarang, Jl. Prof. H. Soedarto S. H., Tembalang, Semarang, Central Java, 50275, Indonesia; [arifwahyudianto@polines.ac.id](mailto:arifwahyudianto@polines.ac.id)

<sup>2</sup> Faculty of Forestry and Tropical Environment, Mulawarman University, Kampus Gunung Kelua Jl. Penajam, PO Box 1013, Samarinda, 75124, Indonesia; [af.andrian.fernandes@gmail.com](mailto:af.andrian.fernandes@gmail.com)

\* Correspondence: [arifwahyudianto@polines.ac.id](mailto:arifwahyudianto@polines.ac.id)

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**Abstract:** Copper radiators are widely used in automobiles due to their high thermal conductivity. However, they are prone to corrosion, which can lead to reduced vehicle performance. This study aimed to identify the chemical components of copper radiator parts and evaluate corrosion inhibition by keruing oleoresin as a natural, eco-friendly coating material. The research involved determining the chemical elements of copper radiator parts using emission spectroscopy and assessing the corrosion rate of copper radiator parts coated with keruing oleoresin in distilled water conditions using electrochemical tests. The results showed that a 5 % concentration of keruing oleoresin provided the best corrosion inhibition, with an OCP of 0.124 V, a corrosion rate of 0.00673 mm/year, and an inhibition efficiency of 88.15 %. The study demonstrates the potential of keruing oleoresin as a natural corrosion inhibitor for copper radiators, helping prevent corrosion and maintain radiator efficiency.

**Keywords:** copper corrosion; corrosion inhibitor; keruing oleoresin; *Dipterocarpus grandiflorus*; electrochemical testing

## 1. Introduction

Copper is commonly used as a material for automobile radiators because of its high thermal conductivity, which allows heat to be easily transferred from the engine to the radiator [1]. The copper material of a heat exchanger often interacts with free radical ions, thus accelerating the corrosion process [2]. Corrosion erodes the metal surface, forming a ravine, a depression that might lead to breakage [3]. In the long run, it will create a hole in the radiator, causing it to leak. The radiator can oxidize and discolour with time, reducing its effectiveness and in turn the vehicle's performance [4]. However, it is easy to repair a copper radiator if a leak does occur.

Radiator coolants are essential for preventing corrosion-induced radiator damage [5]. They lose their corrosion-inhibiting capabilities if they are used inadequately or in degraded conditions, increasing the likelihood of corrosion. Water accelerates this process as it possesses a high oxygen concentration and conductivity [6]. Combining a radiator coolant and a corrosion inhibitor helps prevent radiator corrosion better [7].

However, it should be noted that the corrosion inhibitor added to the radiator coolant should be limited in amount, as this may increase the coolant concentration to a harmful level.

Applying a corrosion inhibitor to the copper's surface, preferably a natural one that is highly eco-friendly, is one method of reducing copper corrosion. Oleoresins are natural coating materials that can be applied to copper [8]. Due to their high viscosity, they require dilution in their application to facilitate the metal coating process. Keruing, a plant species from the genus *Dipterocarpus* that is available in abundance in Kalimantan's lowland tropical rainforests, is one of the sources from which oleoresin can be obtained. Keruing oleoresin can be used as an aluminum 1100 coating with an IE of 46.65 % [9]. Phenolic compounds present in *Dipterocarpus* oleoresin serve as active components in natural coatings that inhibit corrosion [10]. Additionally, caryophyllene, a natural terpene found in many plants, including keruing, helps prevent corrosion, especially in acidic settings [11]. It works by adsorbing onto metal surfaces, lowering the rate of corrosion [12].

Keruing oleoresin is insoluble in water [13]; therefore, an emulsifier, such as carboxymethyl cellulose (CMC), is required when using it as a radiator coolant. CMC can link the water surface with oil or oleoresin when applied at a concentration of 7 % at the most [14]. Additionally, it is capable of facilitating fluid heat transfer [15].

The efficacy of oleoresin from olive oil as an inhibitor is demonstrated by its ability to uniformly coat and protect all copper surfaces in acidic environments [16]. Copper surfaces treated with IOS (Oil-Infused Surface) inhibitors exhibit a reduced polarization curve and a lower corrosion rate in sea water compared to bare copper surfaces [17]. Unfortunately, the use of keruing oleoresin as a copper corrosion inhibitor has never been studied. Therefore, this study aimed to identify the chemical components of copper radiator parts, determine the corrosion rate of copper radiator parts coated with keruing oleoresin under distilled water conditions, as indicated by the polarization curves, and identify metal surface damage using SEM EDX.

## 2. Materials and Methods

The materials used in this research were copper radiator parts. Samples of copper radiator parts were analyzed using emission spectroscopy to determine their chemical compositions [18]. Emission spectroscopy was conducted using BRUKER Q2 ION, with an uncoated CCD with a low dark current detector. The spectral range spanned from 170 nm to 685 nm. Flat-field grating that was argon-purged was utilized for a high-transparency optical system, with a 30-pm resolution. The ELEMENTAL SUITE software was utilized for routine operations, quality assurance, and grade identification.

Corrosion inhibitors were prepared by mixing water with 5 % carboxymethyl cellulose (CMC) as an emulsifier [14] and keruing oleoresin at concentrations of 0 %, 2.5 %, 5 %, 7.5 %, and 10 % as a green corrosion inhibitor [19]. Specimens were prepared by cutting copper radiator parts into small pieces 10 mm x 10 mm x 2 mm in dimensions. These specimens were then immersed in the corrosion inhibitors for one hour, dried for one day, and subsequently subjected to electrochemical testing. Each treatment was carried out with three replications.

Electrochemical investigations were performed with a distilled water solution as a corrosion medium. A potentiostat/galvanostat (PGSTAT101) was used to obtain anode and cathode polarization curves [20] for coated copper radiator parts with different concentrations of corrosion inhibitor at 27 °C. Analysis was conducted using the CorrTest software for Windows, versions V6.3.905.8 and V3.5.221109.3, with a serial number CS310M22111234. The electrochemical testing method used 3-electrode cells, with an Ag/AgCl reference electrode and a platinum counter electrode. The applied scan rate was 10 mV/s. Corrosion polarization curves

and a corrosion rate table of copper radiator parts were created. The corrosion rate table includes OCP, I-corr, Ecorr, corrosion rate, and percentage of inhibitor efficiency [21]. OCP was obtained from  $E-t$  (open circuit potential vs. time) measurements. Ecorr corresponds to the potential at  $I = 0$  derived from the potential dynamic polarization (Tafel) curves.

Assessment of the corrosive impact on steel surfaces was performed following electrochemical testing utilizing scanning electron microscopy (SEM) alongside energy-dispersive X-ray (EDX) spectroscopy [22]. SEM EDX was conducted using THERMO FISHER SCIENTIFIC Phenom ParticleX, with 160x–200,000x magnification, 5 kV, 10 kV, and 15 kV acceleration voltages, a Backscattered-Electron-Detector (BSD), a Silicon Drift Detector (SDD) EDX system, an elements B to Am detection range, and Mn  $K\alpha \leq 132$  eV. The intrinsic susceptibility of metallic surfaces to anodic corrosion and the critical mechanism of material deterioration underscore the imperative for the formulation of sophisticated preventative measures [23].

### 3. Results and Discussion

#### 3.1. Chemical composition of copper radiator parts

The chemical composition of the copper radiator parts is shown in Table 1.

**Table 1.** Chemical composition of copper radiator parts

Chemical elements	Sample test results	
	Element content/%	Standard Deviation/%
Cu	99.370	
Zn	0.129	0.036
Pb	< 0.050	0.011
Sn	0.148	0.018
P	0.027	0.006
Mn	0.012	< 0.000
Fe	0.037	< 0.000
Ni	0.057	0.038
Si	0.005	0.002
Al	0.020	0.005
As	0.024	
Bi	< 0.010	
Se	0.053	
Sb	0.093	
Cr	< 0.005	

Based on Table 1, the copper samples contained 99.37 % copper (Cu), and the remaining 0.63 % consisted of metal impurities. For comparison, pure copper contains 99.99 % Cu, 0.0001 % Zn, 0.0025 % Pb, and 0.0037 % Al [24]. Pure copper is considered to be an optimal choice for fabricating radiators, heat exchangers, and cooling systems due to its superior thermal conductivity [25]. Copper impurities, including aluminum (Al), tin (Sn), and zinc (Zn), enhance its mechanical characteristics but dramatically diminish its thermal conductivity [26]. Meanwhile, the elements Cr and Ni independently affect its heat resistance and recrystallization temperature conductivity [27].

Pure copper contains impurities such as silicon (Si), tin (Sn), aluminum (Al), nickel (Ni), iron (Fe), and titanium (Ti) [28]. As an impurity, zinc (Zn) corrodes more quickly than copper due to differences in electrical potential [29]. Chromium (Cr) should have its concentration in copper metal minimized, as it might exacerbate corrosion [30]. Tin (Sn), another impurity in copper metal, promotes corrosion by causing early cracking [31].

3.2. Electrochemical test results

The polarization curves based on the electrochemical test results for copper radiator parts coated with oleoresin in a distilled water medium are presented in Figure 1.

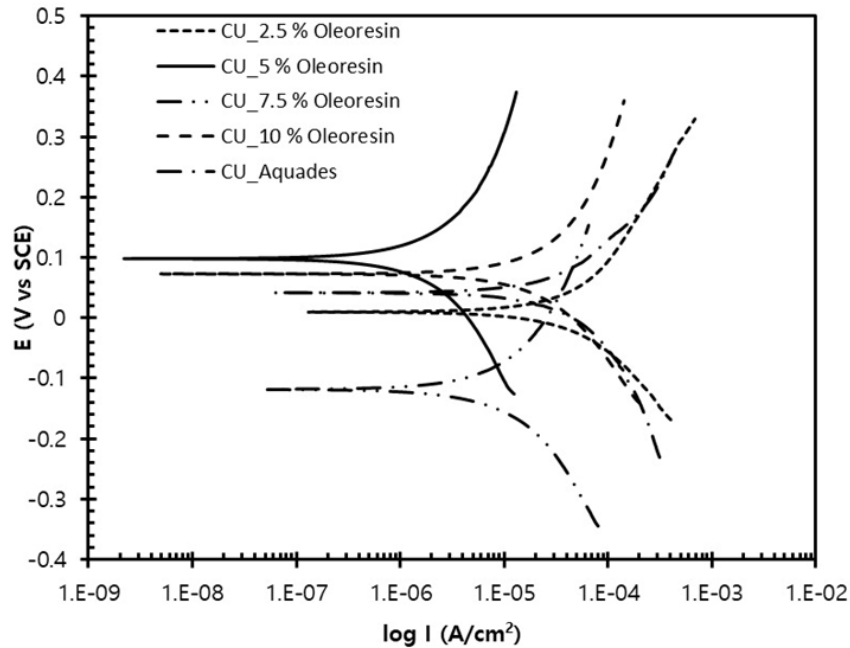


Figure 1. Corrosion polarization curves showing the effect of oleoresin concentration on the corrosion of copper radiator parts

One essential electrochemical metric for evaluating corrosion characteristics is the sample polarization curve [32]. The Tafel diagram is altered by a corrosion inhibitor coating when compared to an unprotected metal surface [33]. According to Figure 1, the Tafel diagram for 5 % indicates the best corrosion inhibition when compared to concentrations of 0 %, 2.5 %, 7.5 %, and 10 %. The ability of an active corrosion inhibitor component to coat metal surfaces may decrease if its concentration is excessively high [34]. For comparison, olive leaf extracts (OLE) at a concentration of 0.76 g/L can be used as a copper corrosion inhibitor under 0.5 M HCl conditions [35]. The results of electrochemical testing of copper radiator parts coated with oleoresin at various concentrations can be seen in Table 2.

Table 2. The effects of various concentrations of oleoresin on the corrosion of copper radiator parts

Oleoresin Conc./%	OCP/V	I-corr/( $\mu$ A/cm <sup>2</sup> )	E <sub>corr</sub> /mV	Corrosion rate mm/year	% IE
0	0.020 ± 0.001	96.33 ± 0.97	0.042 ± 0.001	0.568 ± 0.003	0.00
2.5	0.081 ± 0.001	76.45 ± 1.02	0.010 ± 0.001	0.451 ± 0.002	20.64
5.0	0.124 ± 0.002	11.41 ± 0.11	0.098 ± 0.001	0.00673 ± 0.00008	88.15
7.5	0.166 ± 0.002	24.22 ± 0.24	0.137 ± 0.002	0.0143 ± 0.0002	74.85
10	0.110 ± 0.002	60.05 ± 0.68	0.726 ± 0.002	0.354 ± 0.003	37.67

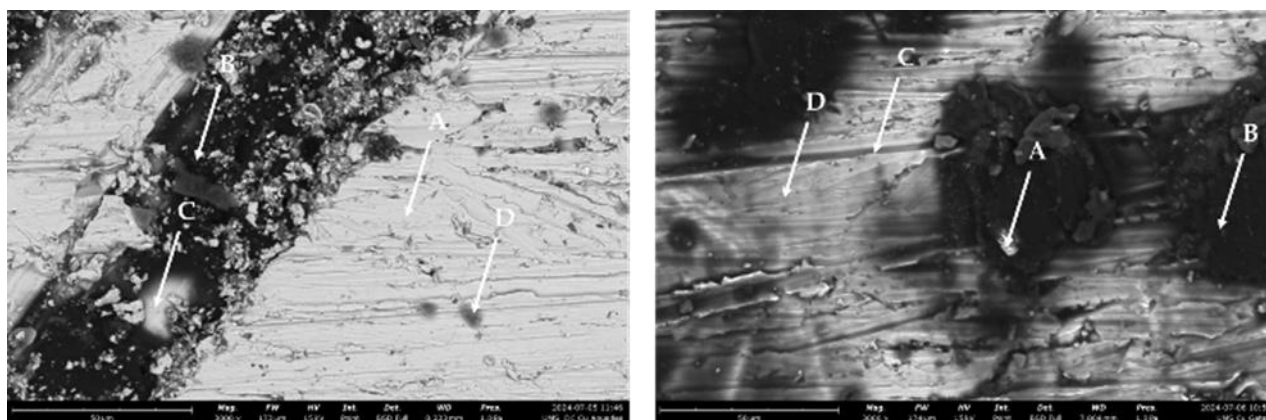
OCP is the potential of the working electrode measured relative to the reference electrode under open-circuit conditions [36]. The lowest OCP on the test sample coated with 2.5 % oleoresin was 0.081 V. For comparison, in a solution containing 10 mM glycine and different concentrations of BI, BTA, and MBI, the OCP–time curve of the copper electrode has a value of roughly 3 mV, or 0.003 V [37]. The OCP of copper coated with acridine orange (3,6-bis(dimethylamino)acridine) (AcO) in a 0.5 M H<sub>2</sub>SO<sub>4</sub> solution is 5 mV [38].

The corrosion rate of copper coated with oleoresin is lower than that of uncoated copper. Oleoresin creates a thin coating that slows down the rate of corrosion [16]. Caryophyllene, the primary component of oleoresin, serves as a corrosion inhibitor [39]. Caryophyllene attached to the metal surface will repel electrons, thus reducing the I-corr value [12]. The presence of caryophyllene, which exhibited intermediate adsorption energies of -46.321 kJ/mol and -49.086 kJ/mol, suggests potential efficacy in corrosion protection [40]. Caryophyllene functions not merely as an anodic or cathodic inhibitor, but as a mixed-type inhibitor that mitigates both, with a slight tendency toward cathodic inhibition [41].

The electrochemical test results presented in Table 2 indicate that copper coated with 5 % oleoresin had the lowest I-corr value and the lowest corrosion rate, being 11.41 μA/cm<sup>2</sup> and 0.00673 mm/year, respectively. For comparison, Cu-ETP with a Cu content of 91.6 %, soaked in distilled water, showed an I-corr value of 10.9 μA/cm<sup>2</sup>, an Ecorr value of 433 mV, and a corrosion rate of 0.133 mm/year in an electrochemical test [42]. Copper C70600 immersed in 0.71 M NaCl has a corrosion rate of 0.04826 mm/year [43].

### 3.3. Changes in the test sample surface after electrochemical testing

The changes in the test sample surface after electrochemical testing can be seen in Figure 2 and Table 3.



**Figure 2.** SEM micrographs after electrochemical testing: (A) 0 % oleoresin coating and (B) 5 % oleoresin coating

**Table 3.** Chemical compound contents based on SEM EDX identification results

Chemical element	0 % oleoresin coating				5 % Oleoresin coating			
	A	B	C	D	A	B	C	D
Cu	52.9	0.7	1.0	1.2	99.3	0.8	2.2	22.7
C	21.4	39.0	23.1	33.7	41.5	83.5	86.7	74.5
O	5.4	12.3	62.9	28.1	0.4	15.1	10.2	2.8
Fe	0.0	0.0	0.0	0.4	0.0	0.0	0.1	0.0
Ni	0.0	0.0	0.0	0.1	0.0	0.0	0.2	0.0
Cr	0.0	0.1	0.0	0.1	0.0	0.0	0.0	0.0

Figure 2 (A) shows that the copper test sample soaked in 0 % oleoresin experienced corrosion, as shown by the formation of a ravine, with a crack width of around 50 μm. Similarly, results of an electrochemical test with a 0.5 M H<sub>2</sub>SO<sub>4</sub> solution showed that copper coated with the anti-corrosion agent 3-chloro-6-mercapto-pyridazine (CMP) sustained corrosion damage in the form of ravines [44]. The corrosion-induced crack pattern

may become a weak point in the metal, and if it becomes too long and too deep, it may cause holes or fractures in the metal [45].

Based on Table 3, the copper surface coated with 0 % oleoresin experienced a decrease in Cu content and possessed a higher O content compared with the copper surface coated with 5 % oleoresin. The corrosion process turns pure metal elements into metal oxides, resulting in a decrease in metal content and an increase in metal oxide content [46]. The element C on the surface of the test sample coated with 0 % oleoresin came from the CMC attached to the surface of the test sample. Meanwhile, on the surface of the test sample coated with 5% oleoresin, the higher C content came from both CMC and the carbon compounds from the oleoresin, such as caryophyllene.

#### 4. Conclusions

The copper samples contained 99.37 % copper, with the remaining 0.63 % composed of metal impurities. Based on electrochemical testing, the oleoresin concentration of 5 % provided the best corrosion inhibition without reducing the ability of the inhibitor to coat the copper metal surface properly, with an OCP of 0.124 V, a corrosion rate of 0.00673 mm/year, and an IE of 88.15 %. The corrosion process resulted in a decrease in Cu content and an increase in O content. Based on the SEM EDX results, the copper test sample soaked in 0 % oleoresin experienced corrosion as shown by the formation of a ravine or cracking.

Based on the results of the study, keruing oleoresin can function as an effective and environmentally friendly corrosion inhibitor, capable of significantly reducing copper corrosion. This study specifically examined the copper material utilized in automotive radiator components. However, alternative radiator materials, such as aluminum, brass, or copper alloys, were not analyzed, despite their prevalent use in contemporary radiator systems.

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