Review Article

Submission Date
27 / 10 / 2023
Admission Date
12 / 12 / 2023

COLOPHONY; Corrosion Inhibitors Agent

KOLOFAN; Korozyon Önleyici Ajan

Ahsen Ezel BİLDİK DAL[1]
Mehmet Emin GÜLE[2]

How to Cite: Bildik Dal, A. E., Güle, M. E., (2023). COLOPHONY; Corrosion Inhibitors Agent. *Journal of Environmental and Natural Studies*, 5 (3), 220-pp. DOI: https://doi.org/10.53472/jenas.1382148

ABSTRACT:

Colophony, also commonly known as rosin, is a solid form of resin obtained from pines and various other plants, predominantly conifers. It is a complex mixture of organic compounds, having a rich history of use in various applications such as the manufacturing of adhesives, varnishes, and soldering fluxes. Remarkably, its properties lend themselves to act as a corrosion inhibitor, a role that has gained increasing attention in materials science and industrial applications. This examination delves into the mechanistic function of colophony as a corrosion inhibitor, explores the diversity of its applications, and critically assesses its efficacy and limitations.

Colophony is considered as green oil because it is a renewable, inexpensive, and environmentally friendly material. The ability of colophony, also named naval store, to improve the sealing properties of ships is a well known feature. In the oil industry, colophony derivatives have a rising interest as corrosion inhibitors thanks to their amphiphilic nature. Additionally, it could be utilized as a petroleum dispersant. Colophony and derivatives as inhibitor agents of metallic surface corrosion and alloy dissolution in corrosive environments were reviewed. The novel approach and basic chemical reactions of the colophony derivatives as a corrosion inhibitor were reviewed. Toxicity research approved that colophony and its derivatives are practically non-toxic components. This evidence has strengthened the reason why colophony is the escalated attention of industrial applications. Therefore, colophony and derivatives are advantageous as a unique raw material of advanced polymer applications compared to toxic corrosion inhibitors. A critical note is that colophony and derivatives do not cause water pollution in the field such as maritime transportation.

KEYWORDS: *Rosin/Colophony; Rosin ester, Corrosion chemicals, Tall Oil Rosin, Gum Rosin*

INTRODUCTION

Colophony is obtained from oleoresin, toll oil, and wood stump sources from the Pine species. The dominant components of colophony are resin acids primarily abietic acid. Colophony derivatives are renewable raw materials which has enhanced solubility and are ambient in nature. Besides, compared to petroleum-based materials it has affordable prices and low toxicity. Nowadays, colophony and derivatives have been investigated for novel applications in various fields as microencapsulation, drug delivery systems, film coating in the pharmaceutical industry, etc. They have deep knowledge in various industrial areas as well such as the paper sizing agent, printing ink, coatings industry, epoxy curing agents, adhesives, etc. As plasticizer agents, colophony derivatives have particular importance in the food industry as well. Colophony and its derivatives also have the potential production of polymer additives. Hence, they could be utilized as a reactive-monomer in polymerization systems.

Colophony was used in the hydrophobicity of wood resins and therefore it was known as "Naval Stores" in the past. The problem of water leakage from naval stores which were made from wood material, was reduced thanks to the colophon coating. The earliest known application of colophony application was to provide resistance to water to naval stores. It is still used in various fields for the same purpose. Resin types obtained by different methods are used for various purposes. Thus, it is convenient to classify each type of resin according to the method of obtainment.

The gum rosin sources of oleoresin are obtained from pine trees that grow in the Mid Altitude regions and China, Brazil, and Indonesia are respectively the world's leading producers. These countries provide more than 90% of the world's gum rosin

[1] **Corresponding Author Yetkili Yazar:** Istanbul University - Cerrahpasa, Forestry Faculty, Department of Forest Products Chemistry and Technology, ahsenezel.bildik@iuc.edu.tr, ORCID: 0000-0002-9525-2993

[2] Chemical Engineering Information Technology Specialist, Edremit, Balikkesir

production (Cunningham, 2012; da Silva Rodrigues-Corrêa, de Lima, & Fett-Neto, 2013). Gum rosin/oleoresin is obtained by tapping the pine trees. An average of 1.5-2 kg of raw oleoresin is obtained from each tree by year. The oleoresin consists of 78-80% rosin, 13-17% turpentine, and the remains of impurity and water. In China, rosin terms represent 'Gum Rosin' products and 661,200 metric tons of gum rosin were produced. China contributed 76% of global gum rosin production itself (European Commission, 2011).

Wood rosin, obtained from wood stump hexane extraction, is produced mainly in America and a small amount in Turkey. Total colophony production globally, which was 1,114,000 tons in 2010, reached 1.2 million tons in 2016. It is estimated that approximately 61% was oleoresin, the remaining approximately 38% was Tall Oil Rosin (TOR) and the remaining other part was Wood Rosin (Cunningham, 2012; Yıldızbaş vd., 2023). CWR (Crude Wood Rosin) composition approximately 85-90% Wood Rosin (colophony), 8-9% Turpentine, 1% Pine Oil (alpha-terpineol), 1% Pine Tar. The wood rosin has a unique composition in that there are some components such as Pine Oil. Also, extractive content increases due to chemical changes after the cutting of a living tree (Weaver, 1983). Pine stumps remaining underground after cutting the living tree both contribute to the economy and provide employment. It is a business that will prevent the forest villagers from leaving their place. The products reduce our foreign exchange output in our imports. It is an industry branch that does not cause environmental pollution and has near zero waste.

Lastly, toll oil is the by-product of the kraft pulp process. Unlike other resin types, toll oil contains fatty acids as well as resin acids. Toll oil rosin (TOR) is a byproduct of the kraft and the USA, Finland, Sweden, France, and Japan are the main countries of production. Wood Rosin (WR) and Tall Oil Rosin (TOR) are also unique products of colophony resources. Having 50% of the world market, the USA is TOR's highest production country. Total rosin/colophony production is 1,250,000 metric tons approximately.

1. Applications of Colophony

1.1. Electronics Industry

In the electronics industry, colophony-based fluxes are frequently employed in soldering to prevent the oxidation of metal surfaces, thereby enhancing the electrical connection between components. It acts as a temporary protective film during the joining process.

1.2. Marine and Coatings Industry

The marine industry deploys colophony as an additive in anti-fouling coatings, which serves the dual purpose of deterring marine organism attachment and curtailing corrosion beneath the waterline on naval vessels and offshore structures.

The concept of inhibitors is an important factor in medicine since the working mechanism of many drugs is based on inhibiting certain enzymes. All of the reactions in the human body take place under the control of certain enzymes.BU cümleler bu başlığa uygun değiller. The reason why we talk about rosin in this article is that it is named as shipbuilding (caulk-dye) material under the name of "NAVAL STORES". In other words, the protection of the surface that it touches against external effects and corrosion by covering certain places. We have very valuable experts, and engineers on this subject. Here we want to try to clinch the place of colophon in the world of Corrosion. The reason for our willingness to do this is that the colophony and derivatives can be produced in Turkey, and to bring our values, which are about to disappear, to light again. The world is moving away from fossil products and embracing natural renewable products. We will prefer the blessings of our soil, sun, forest, and pine trees over synthetics. As natural products, it should be to investigate rosin, synthesis, and characterization of several bio-based surfactants and develop the application goal. Bu cümleler de bu makalenin amaçlarını anlatıyor. Yine ayrı bir başlık altında olmalı diye düşünüyorum.

The corrosion prevention of RPEG600 and RLA-PEG600 compounds on the surface of the steel could be measured by EIS (electrochemical impedance spectroscopy) and electrochemical polarization technique. Results of electrochemical data, both compounds suppress the anodic and cathodic reactions. Besides behavior??? mainly as a mixed type of inhibitor. The researchers have been fixed by experiments and measurements where it has shown that the corrosion inhibition of the steel is highly dependent on the molecular structure and the concentration of inhibitors.

1.3. Petroleum Industry

The petroleum industry applies colophony as a constituent in pipe thread compounds and as an inhibitor in acidizing fluids for well-stimulation purposes. Its ability to form a film over metallic surfaces helps to protect the structural integrity of the installations in aggressive environments.

1.4. Colophony – Based Polymer as Film Coating Agents

Diclofenac sodium as a coating material of pellets in the drug model, provides controlled release of the medicine (Mandaogade, Satturwar, Fulzele, Gogte, & Dorle, 2002). Blending colophony with dibutyl phthalate and polyvinyl pyrrolidone produces a smooth film with higher elongation and tensile strength (Sheorey & Dorle, 1991). Colophony polymer has been used as a drug delivery system for a while likewise colophony esters such as penta erythritol colophony ester gum production researches as drug coating materials (Pathak & Dorle, 1986, 1987). In addition, Sahu et al. (Sahu, Mandaogade, Deshmukh, Meghre, & Dorle, 1999), rosin-glycerin ester while carrying out valuable in vivo biodegradation studies of its derivative researched the drug kinetics of rosin- glycerol ester microcapsules (Sheorey & Dorle, 1990, 1991). Satturwar et al. (Satturwar vd., 2002) used some resin-based polymers as film coating material synthesized and evaluated. Likely, resin-coated microspheres for sustained release of aceclofenac were researched (Prabu, Shirwaikar, Shirwaikar, & Kumar, 2009).

1.5. Mechanism of Colophony as a Corrosion Inhibitor

The underlying principle of corrosion inhibition is the reduction or prevention of oxidation-reduction reactions on metal surfaces, which are the primary mechanisms in material degradation. Corrosion inhibitors, such as colophony, exhibit this protective behavior through multiple pathways, including adsorption onto the metal surface, formation of a protective thin film, or modification of the corrosive environment.

Colophony contains several resin acids, such as abietic acid and its isomers, which are characterized by their hydrophobic backbones and dissociable carboxylic acid groups. These molecules can adsorb onto metal surfaces, particularly those undergoing oxidative corrosion in aqueous environments. The adsorption typically involves both physisorption, driven by Van der Waals forces, and chemisorption, involving the exchange or sharing of electrons between the inhibitor molecules and the metal surface. The presence of electron-rich areas within the resin acids facilitates the adsorption process, further enhancing the inhibitory effect.

Once adsorbed on the metal surface, the resin acids in colophony coalesce, forming a protective layer that impedes the ingress of corrosive agents, such as water, oxygen, and chloride ions. This barrier function is of paramount importance in environments where the presence of aggressive species accelerates the degradation of materials.

Corrosion poses an obstacle to the use of metals as mild and carbon steel and they are widely used in marine applications, especially in salty water. In such cases, replacing alternative inhibitors with non-toxic and inexpensive inhibitors that require a stringent synthesis process is emphasized by various researchers (Izionworu, 2020). Hence, synthesis of corrosion inhibitors from natural sources have received growing interest (Chirkunov, Kuznetsov, & Gusakova, 2007; Quraishi, Jamal, & Saeed, 2000). Various future trends for colophony derivatives as corrosion inhibitors are also commented that polyesters derived from colophony maleic anhydride additive as corrosion inhibitors for steel (Atta, Nassar, & Bedawy, 2007). In addition, dehydroabietylamine and its corresponding ammonium salts have a variety of applications from anti-corrosion agents, antioxidants, fungicides, and flotation agents (Zinkel, 1989).

Structurally equivalent to those water-soluble polyamides and poly (amide-imides) and poly-hydroxyimides have been proposed as carbon steel corrosion inhibitors (Mustată & Bicu, 2009). The corrosion prevention effectiveness of 6 water-soluble resin-based inhibitors for decreasing aluminum and steel corrosion rates in seawater was researched. The weight loss of the samples after prolonged immersion in inhibitors correlated with corrosion rates containing artificial seawater at the dosages recommended by the developer (Lambrakos, Trzaskoma-Paulette, Cooper, & Tran, 2004).

The basic definition of an inhibitor is that substances that reduce the effectiveness of chemical reactions. Enzyme inhibitors slow down reactions by binding to enzymes. Inhibitors are mainly the subject of chemistry. Because their main function is to slow down or stop chemical reactions. Many reactions in chemistry have their inhibitors. The effect that reduces the effectiveness of chemical reactions and prevents enzymes from binding to the target molecule is called an inhibitory effect. The mechanism of the inhibitor alternatives is also highlighted.

The concept of inhibitor appears in various novel applications (Kim, Karayan, Milla, Hassan, & Castaneda, 2020). It is possible to answer the question of what an inhibitor is in various fields such as construction in petroleum in salty environments, oil refining, chemical processing, and marine applications besides medicine, chemistry, and biology. Organic natural polymers as colophony derivatives could be used as polymers complex to develop the efficiency of inhibitors that have synergistic effects with surfactants and halide ions (Izionworu, 2020).

The surfactants prepared had elevated emulsification (emulsifier) activity and high foam stability (Jin, Li, Li, & Zhang, 2011). Colophony and derivatives are often utilized as surfactants with various chemical structures examples of colophony raw material could be transformed the rosinyl amine salt surfactant. Polymers from the resin acrylic-acid additive have also been used as emulsifiers to stabilize regenerated petroleum emulsions (Sinha Roy, Kundu, & Maiti, 1990). Researchers prepared various surfactants from bioresources like cellulose lignin and colophony (Assessment, 2009), and the compounds were evaluated as emulsifiers of crude oil. Rosin-based nonionic surfactants are currently utilized as emulsifiers (Lim, 2009).

1.6. Efficacy of Colophony

Empirical and analytical studies have substantiated the potency of colophony as a corrosion inhibitor. Its effectiveness is contingent on various factors, including concentration, pH of the environment, and the nature of the metal substrate. The adsorption of colophony molecules on the metal surface often follows a Langmuir adsorption isotherm, which suggests a monolayer coverage and implies strong inhibitor-substrate interaction.

1.7. Advantages

- **Environmental Considerations**: Colophony is a naturally derived substance, potentially offering an environmentally friendlier alternative to conventionally employed synthetic inhibitors.
- **Economic Viability**: Obtained from pine tree stumps and as a byproduct of other processes, colophony presents a cost-effective option for industries.
- **Effective Barrier Formation**: It creates an efficient barrier against various corrosive agents, making it suitable for dynamic and challenging conditions.

1.8. Limitations

Despite its apparent benefits, the application of colophony as a corrosion inhibitor is not without limitations. These constraints are worth considering for a balanced view.

- **Stability**: The thermal stability of colophony may be a concern at elevated temperatures, limiting its applicability in high-temperature environments.
- **Solubility**: Depending on the solvent medium, the solubility of colophony can affect the uniformity of the inhibitory film formed on the metal surface.
- **Specificity**: Its efficacy can show significant variability depending on the metal involved and the corrosion mechanism.

1.9. Counterarguments and Critical Perspectives

Critics may argue that synthetic corrosion inhibitors typically demonstrate more consistent performance profiles and targeted action than naturally-derived alternatives like colophony. Some may raise concerns regarding the possible leaching of colophony-based inhibitors into the environment, possibly leading to chemical degradation products with uncertain ecological impacts.

However, the evolving regulatory landscape and heightened environmental awareness have propelled research into bio-based inhibitors like colophony. Furthermore, advances in the chemical modification of colophony constituents have witnessed improvements in their solubility and thermal stability, addressing some of the previously mentioned limitations.

1.10. Future direction

There is wide attention on synthetic biodegradable polymers (Fomin & Guzeev, 2001; Loshadkin, 2002). Materials obtained from natural polymers from biodegradable raw materials also attract increasing attention. Colophony-based plastics take a special place. Colophony is biologically fragmented. It is a product that can be used, has an affordable price, and is obtainable. Synthesis of nano or micro-size polymer applications of novel material (Fomin & Guzeev, 2001; Loshadkin, 2002). It has attracted more and more attention due to its broad applicability in technologically advanced fields.

CONCLUSIONS

Colophony is a well-known sustainable natural product that has an increasing demand in industrial utilization which has driven scientist's efforts to replace petroleum-based products to reduce negative environmental impacts and conserve natural resources. Regarding this, colophony and derivatives have been used in numerous applications, especially directly contacting soil, water, or living organisms. Colophony is a strong candidate for chemical modification by a chemical process performed on functional groups. Besides being a corrosion inhibitor, colophony application gave promising resources for sustainable natural products with non-toxic features. In this context, converted-based corrosion inhibitors obtained from natural sources will be replaced by toxic-based ones.

In summary, colophony emerges as a compelling option within the pantheon of corrosion inhibitors. With its favorable economic and ecological profile, its employment across diverse sectors underscores a pragmatic convergence of traditional knowledge and modern industrial needs. While it exhibits certain limitations, ongoing research is poised to unlock its full potential, tailoring its performance to meet the demanding specifications of modern applications. As the body of evidence grows in favor of eco-friendly materials, colophony will continue to assert its relevance in the proactive stewardship of material longevity and efficiency.

REFERENCES

Abdel-Raouf, M. E.-S., & Abdul-Raheim, A.-R. M. (2018). Rosin: Chemistry, Derivatives, and Applications: a Review. BAOJ Chemistry, 4(1), 1–16.

Assessment, U. E. N. C. for E. (2009). Polymers and Surfactants on the Basis of Renewable Resources.

Atta, A. M., Nassar, I. F., & Bedawy, H. M. (2007). Unsaturated polyester resins based on rosin maleic anhydride adduct as corrosion protections of steel. Reactive and Functional Polymers, 67(7), 617–626. https://doi.org/10.1016/J.REACTFUNCTPOLYM.2007.04.001

Chirkunov, A. A., Kuznetsov, Y. I., & Gusakova, M. A. (2007). Protection of Low-Carbon Steel in Aqueous Solutions by Lignosulfonate Inhibitors. Protection of Metals, 43(4), 367–372.

Cunningham, A. (2012). Pine Resin Tapping Techniques Used Around the World. Pine resin: biology, chemistry and applications, 1–8.

da Silva Rodrigues-Corrêa, K. C., de Lima, J. C., & Fett-Neto, A. G. (2013). Oleoresins from pine: Production and industrial uses. Natural Products: Phytochemistry, Botany and Metabolism of Alkaloids, Phenolics and Terpenes, 4037–4060. https://doi.org/10.1007/978-3-642-22144-6_175/COVER

European Commission. Directorate-General for Economic and Financial Affairs. (2011). European economic forecast, Spring 2011, 234.

[8]. Fomin, V. A., & Guzeev, V. V. (2001). Biodegradable Polymers, State of the Art and Prospectives of Application. Plast. Massy, 2, 42–48.

Izionworu, V. (2020). Green and eco benign corrosion inhibition agents Alternatives and options to chemical based toxic corrosion inhibitors. Chemistry International. https://doi.org/10.5281/ZENODO.3706592

Jin, Y., Li, S., Li, S., & Zhang, L. (2011). Synthesis and Characterization of Rosinyl Amine Salt Surfactant. Advanced Materials Research, 183–185, 1888–1891. https://doi.org/10.4028/WWW.SCIENTIFIC.NET/AMR.183-185.1888

Kim, C., Karayan, A. I., Milla, J., Hassan, M., & Castaneda, H. (2020). Smart Coating Embedded with pH-Responsive Nanocapsules Containing a Corrosion Inhibiting Agent. ACS Applied Materials and Interfaces, 12(5), 6451–6459. https://doi.org/10.1021/ACSAMI.9B20238/ASSET/IMAGES/MEDIUM/AM9B20238_0011.GIF

Lambrakos, S. G., Trzaskoma-Paulette, P. P., Cooper, K. P., & Tran, N. E. (2004). Properties and effects of water-soluble inhibitors on the corrosion rates of structural metals. Journal of Materials Engineering and Performance 2004 13:6, 13(6), 766–774. https://doi.org/10.1361/10599490421556

Lim, H. N. (2009). Palm-based nonionic surfactants as emulsifiers for high internal phase emulsions.

Loshadkin, D. V. (2002). Biodegradable Plastics: Types of Materials, Their Basic Properties, and Prospective Industrial Applications. Plast. Massyv, 7, 41–44.

Maiti, S., Ray, S. S., & Kundu, A. K. (1989). Rosin: a renewable resource for polymers and polymer chemicals. Progress in Polymer Science, 14(3), 297–338.

Mandaogade, P. M., Satturwar, P. M., Fulzele, S. V., Gogte, B. B., & Dorle, A. K. (2002). Rosin derivatives: novel film forming materials for controlled drug delivery. Reactive and Functional Polymers, 50(3), 233–242. https://doi.org/10.1016/S1381-5148(01)00117-1

Mustată, F., & Bicu, I. (2009). Polyhydroxyimides from resinic acids. Polimery/Polymers, 45(4), 258–263. https://doi.org/10.14314/POLIMERY.2000.258

Pathak, Y. V., & Dorle, A. K. (1986). Evaluation of Pentaerythritol (Rosin) Estergum as Coating Materials. Drug Development and Industrial Pharmacy, 12(11–13), 2217–2229. https://doi.org/10.3109/03639048609042631

Pathak, Y. V., & Dorle, A. K. (1987). Study of rosin and rosin derivatives as coating materials for controlled release of drug. Journal of Controlled Release, 5(1), 63–68. https://doi.org/10.1016/0168-3659(87)90038-1

Prabu, S. L., Shirwaikar, A., Shirwaikar, A., & Kumar, A. (2009). Formulation and evaluation of sustained release microspheres of rosin containing aceclofenac. Ars Pharmaceutica, 50(2), 1–12. Tarihinde adresinden erişildi https://researcher.manipal.edu/en/publications/formulation-and-evaluation-of-sustained-release-microspheres-of-r

Quraishi, M. A., Jamal, D., & Saeed, M. T. (2000). Fatty acid derivatives as corrosion inhibitors for mild steel and oil-well tubular steel in 15% boiling hydrochloric acid. Journal of the American Oil Chemists' Society, 77(3), 265–268. https://doi.org/10.1007/S11746-000-0043-3

Sahu, N. H., Mandaogade, P. M., Deshmukh, A. M., Meghre, V. S., & Dorle, A. K. (1999). Biodegradation Studies of Rosin-Glycerol Ester Derivative. http://dx.doi.org/10.1177/088391159901400405, 14(4), 344–360. https://doi.org/10.1177/088391159901400405

Satturwar, P. M., Mandaogade, P. M., Fulzele, S. V., Darwhekar, G. N., Joshi, S. B., & Dorle, A. K. (2002). Synthesis and evaluation of rosin-based polymers as film coating materials. Drug development and industrial pharmacy, 28(4), 381–387. https://doi.org/10.1081/DDC-120002999

Sheorey, D. S., & Dorle, A. K. (1990). Preparation and in vitro evaluation of rosin microcapsules: solvent evaporation technique. Journal of microencapsulation, 7(2), 261–264. https://doi.org/10.3109/02652049009021839

Sheorey, D. S., & Dorle, A. K. (1991). Release kinetics of drugs from rosin-glycerol ester microcapsules prepared by solvent evaporation technique. Journal of microencapsulation, 8(2), 243–246. https://doi.org/10.3109/02652049109071492

Sinha Roy, S., Kundu, A. K., & Maiti, S. (1990). Polymers from renewable resources—13. Polymers from rosin acrylic acid adduct. European Polymer Journal, 26(4), 471–474. https://doi.org/10.1016/0014-3057(90)90055-9

Weaver, J. C. (1983). Kirk-Encyclopedia of Chemical Technology. (H. F. Mark, D. F. Othmer, C. G. Overberger, & G. T. Seaborg, Ed.) (John Wiley). New York.

Yıldızbaş, A., İstek, A., Burcu SIRADAĞ, C., Üniversitesi, B., Fakültesi, O., Endüstri Mühendisliği Bölümü, O., Eğitim Enstitüsü, L., & Endüstri Mühendisliği Ana Bilim Dalı, O. (2023). Reçine Üretimine Genel Bir Bakış ve Covid-19' un Üretim Üzerine Etkisi. Bartın Orman Fakültesi Dergisi, 25(2), 320–339. https://doi.org/10.24011/BAROFD.1218040

Zachary, L. G., Bajak, H. W., & Eveline, F. J. (1965). Tall Oil and Its Uses. New York: McGraw Hill.

Zinkel, D. F. (1989). Naval Stores. Içinde J. W. Rowe (Ed.), Natural Products of Woody Plants (ss. 953–978). Berlin, Heidelberg: Springer.