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A Review on the Transition and Inner Transition Metallic Soaps

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Abstract: A review of the metallic soaps, preparation, mechanism, and their physicochemical properties in solid state as well as in solution. The properties of metallic soaps, including their state, stability, reactivity, volatility, and solubility in common solvents, are key factors that determine their potential applications and uses. The suitability of metallic soaps for specific purposes depends on their ability to meet the necessary physical requirements for a given application, such as their ability to remain stable under certain conditions or their solubility in specific solvents. By understanding these physical characteristics, researchers and industry professionals can determine the most effective ways to utilize metallic soaps in a variety of applications, from cosmetics to pharmaceuticals to industrial processes. This review highlights the diverse range of circumstances in which metallic soaps can be formed. These situations may involve composite objects made up of various materials containing fatty acids such as leather, and wood, in the presence of metals, metal alloys, or pigments. The formation of these metal soaps can occur in a variety of situations, which are explored in this collection.
***Keywords*: Metallic soaps, Surfactants, Mechanism, Applications.**

I. INTRODUCTION

Soap is a type of organic salt that consists of a metal cation and a carboxylate anion. The alkyl chain in the carboxylate anion contains eight or more than eight carbon atoms [1]. However, it is commonly understood that only the alkaline salts of sodium, potassium, and ammonia meet the specific criteriato be classified as "soap". Other metallic salts, while technically classified as soaps, are not typically referred to as such in common usage [2]. Similarly, other types of carboxylates are formed from various metal cations and differ from alkaline soaps due to their insolubility in water and higher solubility in non-polar solvents. These carboxylates may have unique properties and applications based on the specific metal cation used in their synthesis [3]. Metallic carboxylates are a diverse group of chemical compounds characterized by the general formula M(RCOO)n, where R represents a long-chain fatty acid.[4]. Metallic soaps are surface active agents that adsorb at the solid's surface. Theinvestigation of metal soaps is gaining significance in technological and academic domains, owing to their distinctive nature resulting from the coexistence of both hydrophilic and hydrophobic components within the same molecule [5]. Metallic soaps possess unique properties that make them highly valuable in various specialized applications. The importance of these soaps in the industry cannot be solely determined by annual production figures, even though their production has increased significantly in recent years. Historically, metallic soaps were developed to improve lubrication, as gels formed from these soaps and petroleum hydrocarbons proved to be excellent lubricants. Over time, the applications of metallic soaps have expanded to hundreds of uses across various industries, including pharmaceuticals, agriculture, textiles, rubber, chemicals, plastics, mining, ore processing, petrochemical production, adhesives, and electroplating. Despite these diverse applications, the selection of metallic soaps for specific purposes largely depends on empirical knowledge and economic factors [6]. This review provides a comparative analysis of various analytical methods used to study metallic soaps. It delves into the benefits and limitations of each method, as well as their applications in analyzing reference materials and samples from metallic soaps. By evaluating the effectiveness of different analytical approaches, researchers can better understand the properties and behavior of metallic soaps and develop more accurate and reliable methods for studying them [7]. The survey of the literature included several researchers [8]-[12] preparing, characterizing, and applications of metal soaps. S. Sutrisno et.al [13] synthesized zinc, aluminum, and magnesium metal soaps through trans-saponification of potassium carboxylate with its chloride salt. The metal soaps derived from both fully saturated and unsaturated fatty acids were prepared by K. Yamaguchi et.al [14] by metathesis of potassium carboxylate with metal salts in the presence of water and an organic solvent. F.P. Rui Pereira [15] and G. Prakash [16] synthesized calcium carboxylates (soaps) by direct metathesis.

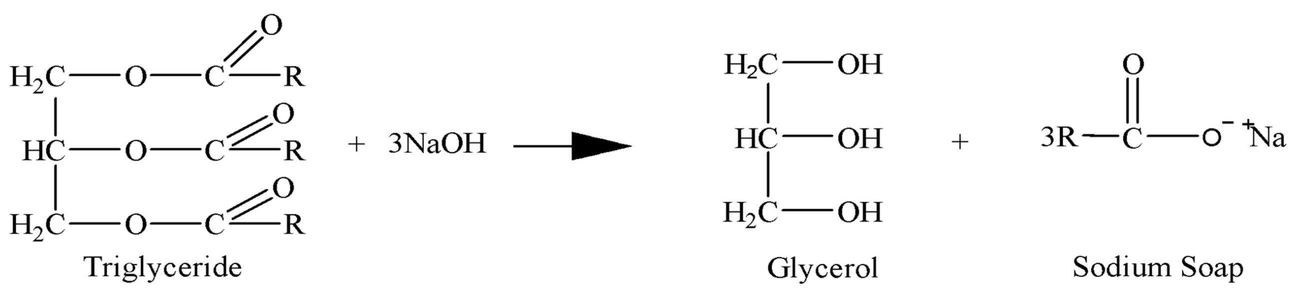
$$RCOOH + NaOH \rightarrow RCOONa + H_2O$$

$$RCOOH + Ca\,(NO_3)_2 \rightarrow \begin{matrix} RCOO \\ RCOO \end{matrix} \!> Ca + 2HNO_3$$

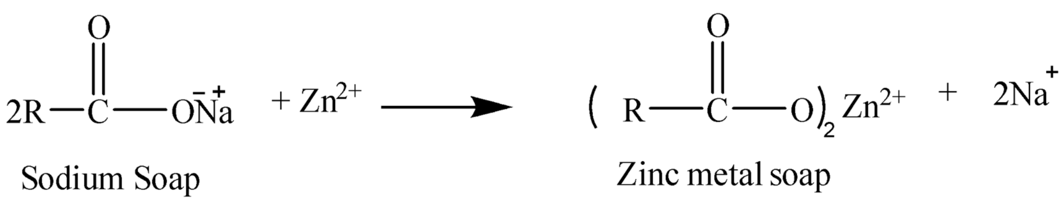
EK Ossai [17] prepared metal soaps of magnesium, calcium (Fig.1), and barium from cocos nucifera seed oil.

Fig.1- Calcium and Magnesium stearate in tablets form

O. Amos et.al [18] synthesized zinc metal soaps from shea butter using the metathesis method.



Saponification of oil to form sodium soap



Precipitation of Zinc soap

V. Chaudhary [19] prepared the molten metal soaps with minimal free acid concentration by stirring andheating the mixture of zinc, cobalt, and manganese oxide or hydroxide suspension. J.B. Owolabi et.al [20] synthesized copper metal soaps from Thevetia peruviana and hura crepitans seed oil. G.Sbringnadello et.al [21] prepared uranium carboxylates by photochemical reduction of corresponding uranium salt while B. Claudel[22] prepared uranium soap by electrochemical reduction. A. Gupta et.al [23] synthesized cerium and thorium soaps by the reaction of an aqueous solution of a metal salt with their potassium soaps. J. J. Hermans et.al [24] reported the kinetics of metal soap crystallization in oil polymers. Sukmawati et.al [25] pointed out that the melting point of metallic soaps depends on the grade of the fatty acid used. This overview provides a comprehensive account of the concepts surrounding the chemical and physical mechanisms implicated in the creation while showcasing prevalent analytical methods used for detecting and studying the distribution of metal soaps.

II. PREPARATION AND MECHANISM OF METALLIC SOAPS

Metallic soaps can be synthesized using two main methods: precipitation and fusion. The precipitation method involves the reaction of a metal salt and a fatty acid in a solution to form a solid residue, whilethe fusion method involves heating the metal salt and fatty acid together until they melt and react [26]. The initial technique involves a double decomposition reaction or metathesis, wherein an aqueous or alcoholic solution containing a soluble salt (such as nitrates, sulphates, or chlorides) of a metal reacts with a soluble alkali salt of the fatty acid. This reaction, which converts one type of soap into another, can also be referred to as "trans-saponification" as it resembles the mechanism of "trans-esterification."[13]. In this procedure, metal soaps manifest as a significantly hydrated residue settling in the solution's lower region.

$$RCOOH + NaOH \rightarrow RCOONa + H_2O$$

$$MNO_3 + RCOONa \rightarrow RCOOM + NaNO_3$$

$$MSO_4 + 2RCOONa \rightarrow R(COO)_2M + Na_2SO_4$$

In the fusion method, the carboxylic acid, oxide, hydroxides, and salt of the desired metal, such as carbonates, nitrates, and acetates, undergo a direct reaction at temperatures ranging from 453K to 573K.

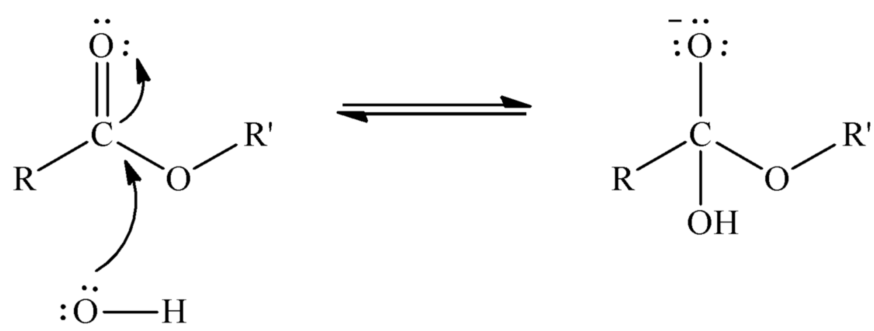
$$2RCOOH + MO \rightarrow (RCOO)_2M + H_2O$$

$$2RCOOH + M(OH)_2 \rightarrow (RCOO)_2M + 2H_2O$$

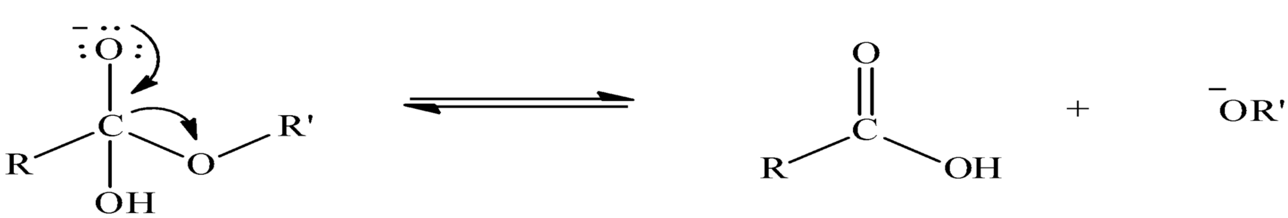
$$2RCOOH + MCO_3 \rightarrow (RCOO)_2M + H_2O + CO_2$$

The general reaction mechanism for acid-catalyzed hydrolysis consists of three main steps [27].

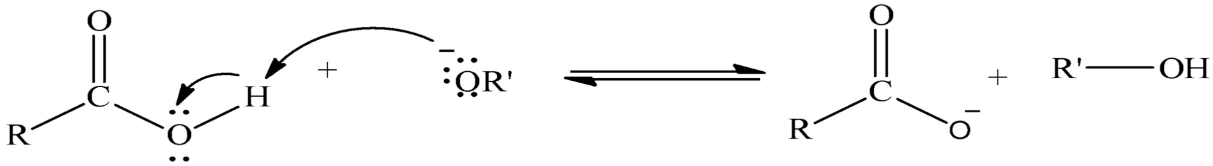
1) *Step 1 - Protonation of the carbonyl group:* In this step, an acid catalyst (such as an H+ ion) donates a proton to the carbonyl oxygen of the substrate. This results in the formation of a tetrahedral intermediate that is more susceptible tonucleophilic attack.



2) *Step 2 - Nucleophilic attack by water:* In this step, a water molecule acts as a nucleophile and attacks the electrophilic carbon atom of the tetrahedral intermediate. This results in the formation of a geminal diol intermediate.



3) *Step 3 - Deprotonation and formation of products:* In this step, a base catalyst (such as -OH ion) deprotonates one of the hydroxyl groups in the geminal diol intermediate, resulting in the formation of a carbonyl compound and a hydroxyl group. The base catalyst also regenerates the acid catalyst by accepting a proton.



Alternatively, the soap manufacturing sector employs the neutralization approach, involving the neutralization of carboxylic acid in the presence of a base to create metal soap derived from transitionand inner transition metals [27].

III.REASONS, FOR THE COMPARISON STUDY

The comparative study of these soaps is almost untouched. Which can explore the new dimension of understanding in their physical and chemical properties, and their uses in several new ways [28]. Metal soaps are a fascinating and complex area of research that continues to evolve to better understand theirproperties and behavior, ongoing studies are exploring various aspects of their formation and degradation. In particular, conservation practices are seeking out new and effective measures for mitigating potential damage from metal soaps. By continuing to investigate the mechanisms behind metal soap formation and their impact on different types of materials, researchers will be better equipped to develop targeted conservation methods that address the unique challenges posed by these compounds [26]. It is important to recognize the potential of metal soaps in various applications, and a comparative study of their properties can help to identify their unique characteristics and potential benefits. Therefore, researchers should aim to investigate and compare the properties of different metal soaps to better understand their potential uses and benefits in various fields. By conducting a comparative study, researchers can gain insights into the unique properties and characteristics of different metal soaps, which can inform the development of new applications and improve the effectiveness of existing ones. The present work deals with the comparative study on physical and chemical properties of following transition and inner transition metal soaps in solid state as well as in solution [29]. Some multiple analytical techniques and methods have been adopted in studying metal soaps. This review provides an overview of various techniques that are commonly used for the identification, localization, and study of metallic soaps. This review aims to familiarize readers with the different methods available for analyzing metal soaps and to highlight the advantages and limitations of each technique. Several researchers [30]-[32] studied the IR, XRD, and TGA of metal soaps.Infrared Resonance spectroscopy is a powerful analytical technique that has been widely used in the study of metal soaps. IR spectroscopy can provide detailed information about the structure anddynamics of metal soaps, including the bonding interactions between metal ions and fatty acid molecules. Additionally, IR spectroscopy can be used to study the mobility of metal ions in metal soapfilms and to investigate the effect of environmental factors such as temperature and humidity on the properties of metal soaps. Overall, IR spectroscopy is a valuable tool for the characterization of metal soaps and can provide important insights into their behavior and properties. K.Ito et.al [33] assigned the important peaks of infrared spectra of lanthanide acetate and propionate using normal vibration of the structural fragments of these compounds. K. Kishore et.al [34] reported IR spectra of terbium myristate and compared it with potassium soap. The IR spectra of praseodymium soaps were investigated by R. Singh et.al [35]. K. N Mehotra et.al [36] studied the IR Spectra of cerium soaps and proposed their partial ionic character. Rodric et.al [37] discussed Infrared absorption spectra and the thermal behavior of samarium soaps of lauric acid and myristic acid.

$$2(RCOO)_3Sm \rightarrow 3RCOR + Sm_2O_3 + 3CO_2$$

In this study, we will compare the solid-state existence of fatty acids with dimeric structure (Fig.2), which results from the intermolecular hydrogen bonding between carboxyl groups of two acid molecules. In contrast, transition and inner transition metal soaps are ionic, and the bond between the metal and oxygen of these soaps is ionic in nature.

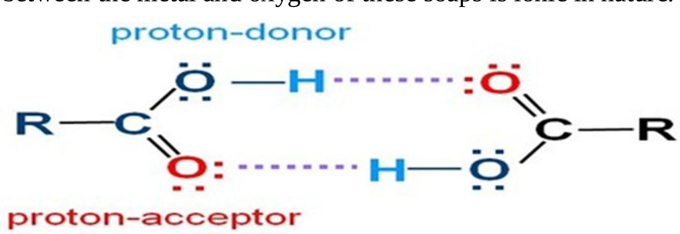


Fig.2 Dimeric structure of fatty acid

The X-ray diffraction studies of metal soaps in the solid state were carried out by researchers [38]-[40]. M. Cotte et.al [41] discussed the XRD of lead carboxylates and suggested a double-layer structure. S.K. Upadhyaya et.al [42] using an x-ray diffraction pattern characterized the double-layer structure of dysprosium soap in the solid state. S.P.S. Saroha et.al [43] used an X-ray diffraction technique to determine the extent of the orientation of soap particles in the grease-like system. In this study, we will compare the soaps that have a double-layer structure (Fig.3). in which the metal ions are arranged in parallel plain and equally spaced in soap crystals.

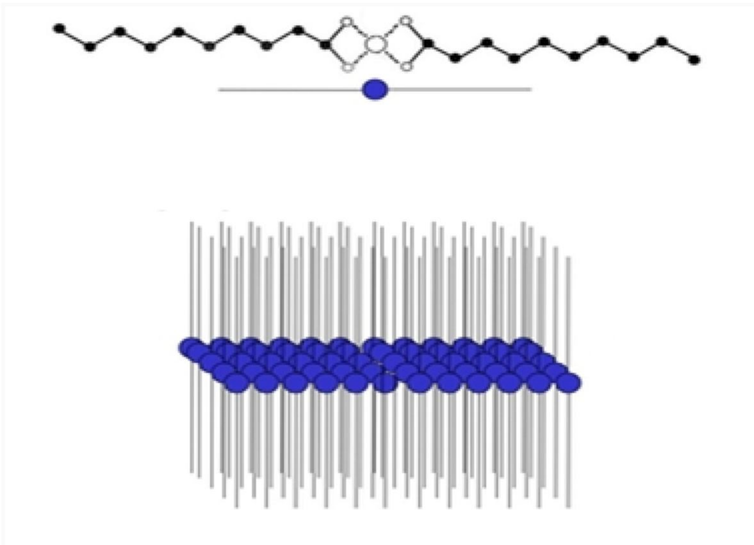


Fig.3 Double-layer structure of metal soap crystal

Several researchers [44]-[49] carried out the thermogravimetric analysis of different metal soaps and reported the order of reaction and energy of activation for their thermal decomposition reaction.S. Kumari et.al [50] reported kinetic study of the thermal decomposition of zinc and cadmium di alkanoates O.M Folarin et.al [51] analyzed the thermal stability of metal soaps of copper, zinc, calcium, barium and calculated the kinetics of decomposition, thermogravimetrically in the range of temperature 160 - 600 0C. B. Gangwar et.al [52] reported the thermalg decomposition reaction of gadolinium soaps and found the reaction of zero order with the energy of activation lying between 26.9–37.6 KJ mol-1. R. Dwivedi et.al [53] calculated the energy of activation for heavy metal soaps. D. Balökse et.al [54] discussed the thermal behavior of barium, calcium, cadmium, and zinc soap from biodegradable rubber seed oil by thermogravimetric analysis. Here we compare to find out the order of reaction and energy of activation for thermal decomposition of metal soaps.

In the solution state Chandrawati [55] discussed micellization behavior and molecular interaction of manganese soaps in different pure and mixed organic solvents by using conductivity, density, and viscosity measurements. S. Kumari et.al [56] studied the conductivity, molar volume, and rheology of samarium soaps in mixed organic solvents. Sangeeta et.al [57] studied the thermodynamics of dissociation and micellization of carboxylates of dysprosium using conductivity results at different temperatures in organic solvents. M. Shukla et.al [58] investigated the thermodynamic behavior of gadolinium alkanoates in a benzene-methanol mixture, they also discussed ultrasonic properties in a mixed organic solvent. C. Chauhan et.al [59] discussed the conductometric studies of neodymium soapsat different temperatures and calculated thermodynamic parameters in a mixture of benzene and dimethyl sulphoxide (60:40 v/v). Conductometric studies on terbium soap solutions were investigated by K. Kishore et.al [60]. The ultrasonic velocity of zirconyl soap in mixed organic solvents was studied by M. Anis [61] and calculated various acoustic parameters A. K. Sharma et.al [62] discussed various acoustic parameters of copper carboxylates. K. N. Mehrotra et.al [63] and Y. Sharma [64] reported ultrasonic results to find out the compressibility behavior of europium soaps in mixed organic solvents, and lithium laureate in a benzene-methanol mixture. The viscosity of cerium soaps innon-aqueous solvents was reported by R. Sharma [65]. The use of zinc and lead soaps as driers in the preparation of paints, varnishes, greases, and other protective coatings was described by T. Poli et.al [66]. S. Khan [67] discussed the viscometric studies of copper surfactants and they calculated various micellar features and solute-solvent interactions in polar and non-polar solvents. M. Gönen et.al [68] characterized the stearate of magnesium, cobalt, and copper and their effects on Polyvinyl Chloride (PVC) Dehydrochlorination.

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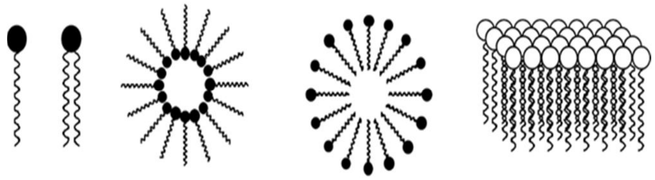
The effectiveness of lauric acid and copper carboxylates as bactericides, herbicides, and fungicides were discussed by Y. Yamamoto et.al [69]. R. Bhutra et.al [70] characterized copper formates derived from soybean and sesame oil by P.D.A. technique.

This review provides a general description of the theories regarding in-solution state we compare conductivity, viscosity, ultrasonic velocity, and scanning electron microscope, to determine the natureof the soaps in a non-aqueous solution and evaluate various acoustic parameters at different temperatures, to find critical micelle concentration, soap solvent interaction. and confirm the value of the CMC shape (Fig.4) and the size of the micelles formed in the soap solution.



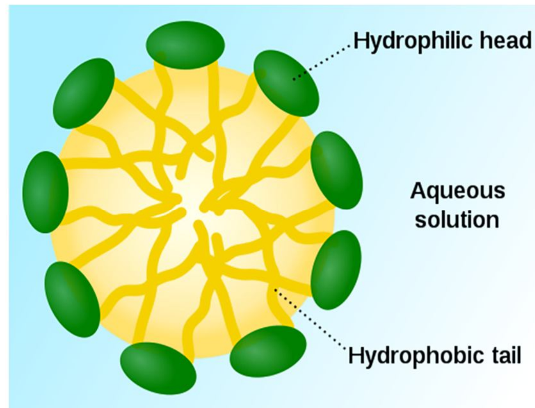


Fig.4 Formation of micelles inverse and reverse

IV. APPLICATIONS OF METALLIC SOAPS

The application of metal soaps depends on their physicochemical properties such as solubility in polar and non-polar solvents, therefore the studies of these soaps are of main importance for their uses in various fields to explain their characteristics under different conditions in solid states and solutions [71]. The hue of metal soaps is predominantly determined by the electronic configuration of the metal cation, which is in turn influenced by the characteristics of the metal. For example, metal soaps containing chromium, praseodymium, nickel, and copper generally appear green, while those containing lead, zinc, aluminum, magnesium, cadmium, and alkali metals typically produce white soaps. Soaps containing manganese and cobalt typically exhibit a lavender hue, while those containingiron generally display red to brown tones. Ascertaining the exact melting points of metal soaps is challenging due to the challenges associated with obtaining these compounds in their purest form. Asa result, the temperature range is typically provided instead of a single melting point value. However, despite this limitation, it is possible to identify trends regarding the melting points of different metal soaps that can be correlated with the properties of the cation [13]. Metal carboxylate molecules have proven to be versatile compounds that can be utilized in various applications. In addition to being used as Functioning agents for water-oil emulsions, and serving as emulsifiers, they are also employed as catalysts in chemical reactions and as stabilizers for polymers. Furthermore, they have been shown to possess antimicrobial properties and are used in pharmaceutical applications as excipients. For example, zinc stearate is commonly used as an excipient in tablets due to its lubricating properties.The unique properties of metal carboxylates make them an attractive option for a wide range of industries, including cosmetics, pharmaceuticals, and materials science. In addition to their use in the manufacture of PVC products, metal soaps are also used in the applications of a variety of other plastics. They are commonly used during the processing of materials such as polyamide, polyethylene, polypropylene, and ABS, as well as in the production of fiber-reinforced plastics. The unique properties of metal soaps, such as their ability to act as stabilizers or catalysts, make them valuable additives in the plastics industry. By incorporating metal soaps into various plastics, manufacturers can enhance the performance and durability of their products [2],[3],[7].

To learn more about the various industrial applications of metal soaps, refer to the supplementary materials. These materials provide a comprehensive overview of the different uses of metal soaps in a range of industries, including adhesives, anti-corrosion coatings, and asphalt modification. By reviewing the supplementary materials, readers can gain a deeper understanding of how metal soaps are used to improve the performance and functionality of various materials and products.

1) *Food Industry:* Surfactants are used as cleaners and emulsifiers in food processing.
2) *Pharmaceutical:* serve as emulsifiers, dispersants, and synergists for active ingredients.
3) *Grease Industry:* Viscosity enhancer in the manufacture of lubricating greases.
4) *Rubber Industry:* Assistance in vulcanization, release facilitator, and lubricating agent.

5) *Stationary:* Uses a lubricant of pencil leads.
6) *Paper Industry:* Lubricant and release agent for sandpaper, chelating agent for pigments.
7) *Metal Industry:* Lubricant and release agent for powder metallurgy, wire drawing,and tube drawing.
8) *Petroleum Production:* Applied in drilling fluids for the dispersion and transportation ofcuttings, as well as for improving oil recovery during production.
9) *Mining and ore processing:* Assisting in binding dust particles and functioning as frothingagents for hydrophobic valuable minerals.
10) *Chemical:* Aid reactivity by their emulsification property, such as in polymerization orhydrolyzed.
11) *Agriculture:* Utilized as emulsifiers (wetting agents) must maintain inertness towardsactive materials. They are required to be biodegradable and exhibit low phytotoxicity.
12) *Plastics:* Widely used in the fabrication of plastic products such as foams, molded items,extrusions, and micro-capsules.
13) *Textile:* Used, to aid in cleaning natural fiber to reduce friction in spinning and weaving [72]-[73]

V. CONCLUSION

Metallic soaps are a multifaceted set of chemical compounds that are made up of fatty acids and alkali metals. These compounds have been used for centuries as cleaning agents due to their unique properties, including their ability to emulsify oils and dirt, as well as their mildness on the skin. Lately,there has been a notable upswing in the attention directed toward metallic soaps due to their potential utility in various industrial sectors, including the manufacturing of biodiesel, textiles, and cosmetics. Additionally, organic soaps have been found to have antimicrobial properties which make them useful as disinfectants in medical settings. The study of metallic soaps and their development is extensively explored within the realm of tribological investigations. These studies have revealed that diverse metal carboxylates can emerge within a lubricant layer during close interaction with a moving metal surface. The objective of this review is to examine the scientific literature that commonly utilized analytical methods for the analysis of metal soaps and compare their effectiveness [7].

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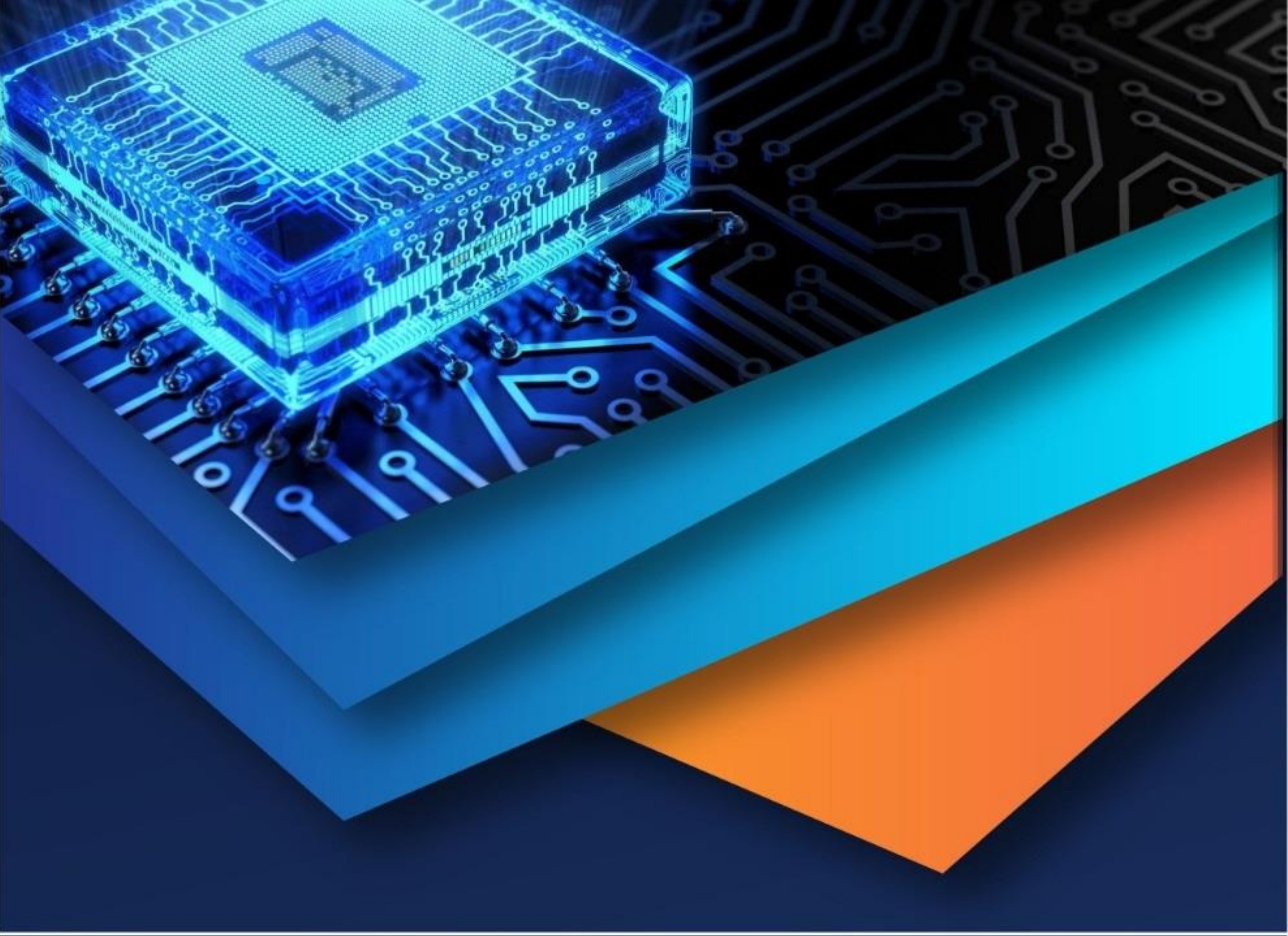

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