

Perspectives of Eco-friendly Anti-Corrosive Coatings

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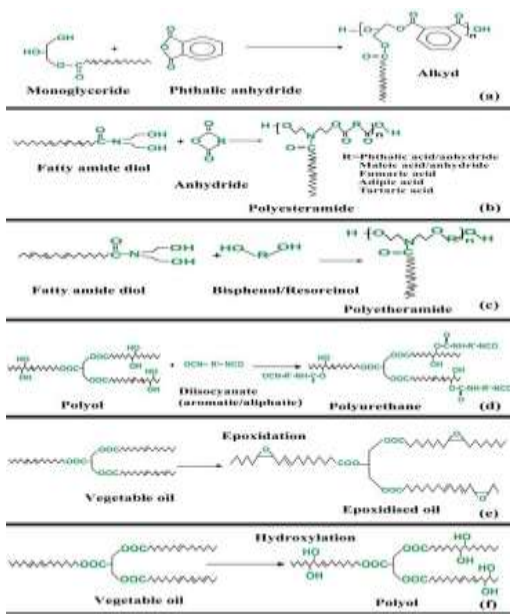
Abstract: The use of vegetable oils in the preparation of polymeric resins is gaining importance. Since ages vegetable oil were used as the primary constituent in paints and coatings. Today, due to several environmental and health hazards from fossil fuel derived products, and fear of depletion of petroleum resources, chemists and technologists have reverted to the extensive utilization of vegetable oil derived materials in paints and coatings. The coating technology holds immense potential globally. Plant seed oils are utilized for preparing polymer-based resin due to its: eco-friendly nature, non-toxicity, biodegradability, reducing the cost of production, solving the problem of waste disposal and unique structure of oil attributes to prepare resins from it so as to provide anti-corrosive, high performance coatings. A part of the review is also dedicated to the future perspectives in the field of coatings.

Keywords: Vegetable oil, Anticorrosive coatings, Health hazards.

1. Introduction

Awareness towards conserving the environment has driven the focus of researchers to develop sustainable and renewable green materials i.e. alternatives for petrochemical based resin, such as epoxy. Petrochemical based resins have better properties such as high stiffness and strength, but have serious drawbacks in terms of biodegradability, high cost, energy consumption and health hazards. Environmental issues and rising price of petroleum has forced to give more attention towards utilization of biodegradable products. As a result, there is a strong need to develop bio-based products from cheaper renewable feedstock. Anti-corrosive coatings have attracted for many years due to its simplicity and efficiency¹⁻³. The

most cost-effective method for metals and alloys protection against corrosion is organic coatings. The metal substrates protection may be attributed to a barrier and an electrochemical process⁴. Organic coatings have a high resistance to ionic conductivity, which can offer good barrier properties⁵ and retard the diffusion of chemical species from the metal surface⁶. Protective coating properties were determined by the rate of water and oxygen diffusion through the insulating layer, promoted by the osmotic pressure in the pores and capillaries of the coating⁷⁻¹¹. Raw materials based on vegetable oils are also important in our life because they have several excellent properties for producing valuable polymers such as polyurethane, alkyd, polyesteramide and epoxy resins, (scheme-1) for example, castor¹²⁻¹⁴, soyabean^{15,16}, sunflower¹⁷, cashew and linseed¹⁸, castor oil¹⁹ and pongamia glabra oil²⁰, have been used for synthesis of different kinds of polymeric materials. Extensive research on the synthesis of vegetable polyols and characterization of their corresponding polyurethane has been carried out²¹⁻³⁰. The fatty acids composition of oil also plays an important role in preparing coatings. Linoleic oils group includes oils containing more than 50% of linoleic acid based upon the total fatty acid content and having iodine values ranging from about 120 to 170. The technical properties may be largely ascribed to linoleic acid, although small proportion of linolenic acid may also be



Scheme 1. Various methods for preparing organic coatings

present. Table-1 gives the latest information about the fatty acid composition of the important members of the group. Soya bean oil is primarily used as edible purpose, but it has also become the most important member of linoleic drying oils. Safflower oil also resembles a high iodine value of soybean oil and is also being used to some extent as a drying oil in India. Other oil of this group that have not yet been produced in sufficient quantities to be of importance in the drying oil industries which include niger seeds (India and West Indies), sunflower seeds (Russia and Argentina), poppy seeds (India) and hemp seed (Russia, France and Italy). Oils with comparable drying properties containing less than 50% of linoleic acid but larger amount of linolenic acid are Candle nut (Fiji, Queensland), rubber seed (South America, Ceylon, Nigeria).

Table 1. Source and composition of important linoleic oils

Oil	Source	% of seeds	Iodine Value range	Fatty acid composition			
				Saturated	Oleic	Linoleic	Linolenic
Soya Bean	Soya Japonica	16-22	125-140	17.2	23.5	49.8	9.5
Tobacco Seed	Nicotiana Tabacum	33-43	135-147	10	15	75	-
Safflower	CarthamusTinctorius	24-36	140-150	9.6	13.4	77	-
Sunflower	Helianthus Annuus	22-32	113-136	14.2	20.9	64.9	-
Grape Seed	VitisVinifera	10-20	133	12	17	71	-
Niger Seed	GulzotiaAbyssinica	38-50	126-135	19.6	6.9	72.7	0.8
Poppy Seed	PapeverSomniferum	44-50	130-140	7.7	30.1	62.2	-
Hemp Seed	Cannabis Sativa	28-35	150-166	16.1	10.8	54.4	18,7
Candle nut	Aleurites Moluccana	55-65	160-165	13.5	14.1	41.6	30,8
Rubber Seed	HeveaBrazillensis	21-25	133-143	23.8	18.4	37.1	20.7

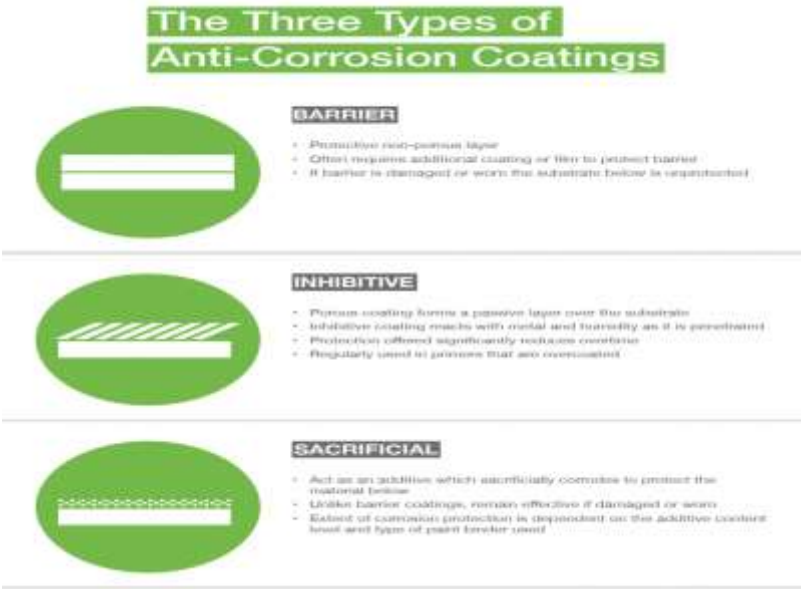
This review aims to examine the state of the corrosion coatings for the protection of various

metals and alloys commonly used in maintenance equipment and vehicles, and to identify cost effective, high-performance corrosion inhibitors that may contribute to the preservation of equipment assets.

2. Anti-Corrosion Coatings and Their Mechanism

Anti-corrosion coatings are vast, but they can be classified (scheme-2) into three main groups:

- (a) **Barrier coatings:** A protective non-porous layer formed over a substrate that prevents the surrounding environment from affecting the base metal. If the coating is applied to the base metal without any other coating or film and the metal is damaged by impact or chemical attack.
- (b) **Inhibitive coatings:** It forms a passive layer on a substrate that reacts with metal and humidity as it penetrates the film. The corrosion protection offered by inhibitive coatings reduces over time, hence these coatings are extensively used in primers that are overcoated.
- (c) **Sacrificial coatings:** It act as an additive over a substrate which sacrificially corrodes to protect the material below. These coatings remain effective if the film is damaged, but the level of protection offered is dependent on the additive content level and type of paint binder used.



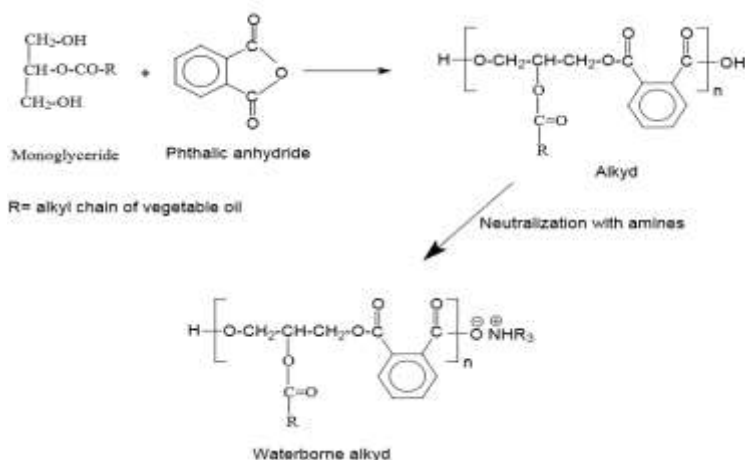
Scheme 2. Types of anti-corrosive coatings

3. Vegetable Oils in Coating Technology

Literature reveals that development of epoxy resin from vegetable oils is gaining importance because of its sustainable, renewable and environment friendly nature. The modified oils can serve as feedstock that can replace petroleum derived materials in many applications. The double bond present in the vegetable oil is used as reactive site to insert various functional groups by carrying out epoxidation reaction which is used to insert the three- member oxirane ring in the unsaturated portion of the oil molecule, which increases its complexity and chemical reactivity with a variety of compounds such as amines and carboxylic acid. The conversion of unsaturation to epoxy groups can be directly monitored by determining the oxirane oxygen content, and indirectly by determining the iodine value. Epoxidation can also be achieved in one step with peroxy acid produced in situ from acetic/formic acid. Enzymatic epoxidation is also being done with the help of specific enzymes. Epoxidized vegetable oils are widely used in polymer industry because of their excellent plasticizing action for poly vinyl chloride and an effective component for stabilizing polymer formulations. Epoxides also find industrial application as diluents, lubricants and coatings³¹⁻³⁸.

Vegetable oils are one of the most important renewable resources for production of polymeric materials like alkyd, polyester amide, polyetheramide, polyurethane, polyester, polyepoxy, and polyamine amide in combination with commercial polymers such as polyvinyl alcohol, polystyrene, polymethylmethacrylate, and polyurethane. Vegetable oil such as linseed, olive, castor, jatropha, soybean, cotton seed etc. are used to produce polymeric coatings³⁹⁻⁴⁹. The utilization of vegetable oil has attracted great attention in both scientific and industrial applications due to easy availability, environmental friendliness, low volatile organic matter, and cost-effectiveness. The vegetable oils which find wide application in surface coating hold considerable promises in this direction because these are the source of unsaturated fatty acids and excellent monomer to produce resinous compounds. The higher the degree of unsaturation the greater the potential for the oil to dry by oxidation to form a cross-linked polymer network. The double bonds also provide site for many other reactions, which are of great importance to coating industries. The selection of oils or fatty acids are made depending on the final use of the resin e.g. whether the resin will be used as film forming materials or as plasticizing materials, like linseed oil used as a drying oil; soybean oil, which do not form satisfactory films at normal temperature, used as a semidrying oil in air drying alkyd resins is

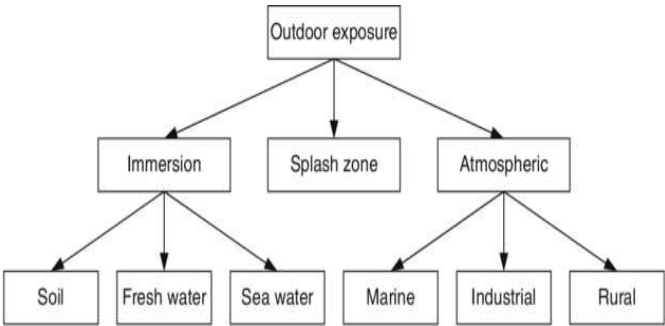
suitable for baking finishes; castor oil, cottonseed and coconut oils are non-drying oils, they cannot form films under air drying or baking conditions; hence they are used as plasticizers⁵⁰⁻⁵⁴. Rice bran oil is polyunsaturated semi-drying oil. One of the oldest polymers prepared from triglyceride oils is polyester resin and traditionally known as alkyd resin. Alkyd resins have acquired a prominent position in paints and coating industries because of their economy, ease of applications and good protection of materials from environmental attacks. Moreover, they are known for biologically degradable polymers as they have repeating ester moieties⁵⁵. The compositions and functionalities of fatty acids play the pivotal role in the properties of alkyd resins, whereas natures of dibasic acids, polyols also significantly affect the properties of the resins (Scheme-3).



Scheme 3. Reaction scheme for vegetable oil based waterborne alkyd

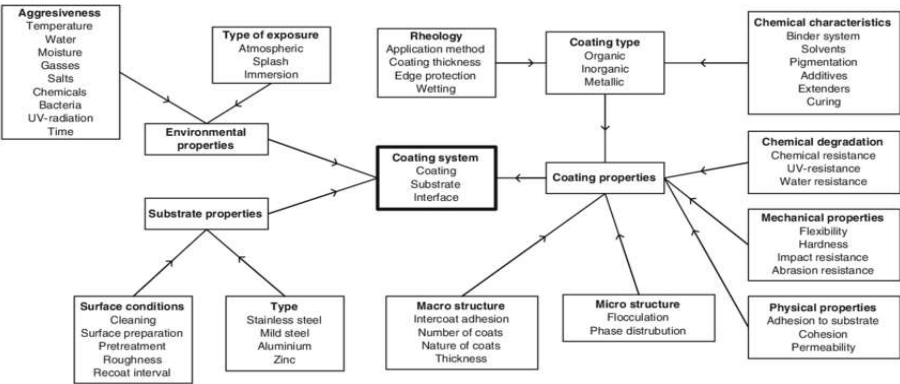
Apart from vegetable oils, intensive research is being done to design a smart and intelligent multifunctional hybrid polymer nano-composite material for emerging applications⁵⁶. Hybrid bio-based materials^{58,59} in contrast to fossil resources have received much attention. They can be produced from many renewable sources. Clay, particularly bentonite, is a naturally abundant resource and environmentally friendly due to its bio degradable and renewable features⁶⁰. Many mechanical properties of polymer materials, such as mechanical strength^{61,62}, tribological performance^{63,64}, thermal stability⁶⁵ and electrical conductivity⁶⁶, can be improved remarkably by incorporating carbon derivatives into polymers. In particular, the antifriction performance of polymer coatings is of practical importance because these coatings are susceptible to damage through scratching and

abrasive wear under outdoor service conditions leading to the loss of mechanical strength. The addition of high-performance nanofillers, such as ceramic particles into polymer coatings, is effective in enhancing their antifriction properties. Anticorrosive coatings are exposed to various environments ranging from constant immersion in water and burial in soil, to atmospheric pollution in industrial areas and ultraviolet radiation (Scheme 4).



Scheme 4. Exposure of Anticorrosive coatings to various environments

In recent years, owing to the growing interest and attention of the world towards the protection of the environment and the hazardous effects of using chemicals on the ecological balance, the traditional approach on corrosion inhibitors has gradually changed (Scheme-5).



Scheme 5. Factors affecting durability of anticorrosive coating system

4. Health Hazards Associated with Paint and Coating Industry

The health hazards have been a source of concern for the paint and coating industry.

- (a) **Volatile Organic Compounds and hazardous air pollutants:** Volatile organic compounds are found in vehicle emissions and anti-corrosion coatings and paints. Their high vapor pressure allows molecules to evaporate into the surrounding air, causing humans to breathe them in as vapors or gases. Hazardous air pollutants are released into the atmosphere and suspect to cause cancer. Compounds including benzene, chlorobenzene, ethylbenzene, acetone, chloroethane, styrene, vinyl chloride, toluene, and xylene are among the common pollutants found in traditional paints and coatings which can cause headaches, dizziness, nausea, and eye or skin irritation. Prolonged exposure also can increase the risk of developing asthma or allergic reactions and could be responsible for more serious and chronic conditions, such as kidney damage and cancer.
- (b) **Flame Resistance:** Many traditional anti-corrosion paints use organic compounds that serve as fuel to a fire in the workplace. These compounds are likely to ignite or melt contributing to the growth of a fire, so they cannot offer flame-spread protection on their own. Traditionally, the solution for companies with carbon steel assets has been to apply a secondary coating that offers flame spread protection. One option to prevent flame spread without using any additional flame retardant is to use a fully inorganic anti-corrosion coating.
- (c) **Microbes, Bacteria and Other Germs:** The danger of microbes on surfaces and substrates, particularly where moisture is present. Consider, for instance, the environments of an offshore oil rig, livestock feeding areas, railroad cars, or freighters and cargo ships. These largely steel structures are breeding grounds for bacteria, viruses, protozoa, and fungi, which can cause allergic reactions to serious health problems for those who work in proximity to them.

5. Moving Towards Safer Coatings

To move towards a safer coating technology, the following parameters are being taken care of today and require further considerations in future.

- (i) Greener isocyanates may be used as green curing agents for vegetable oil coatings.

- (ii) The use of low volatile organic compounds or water as solvent in coatings is another environment friendly approach.
- (iii) Advantages should be taken of inherent fluidity of vegetable oil that may result in the development of low or no volatile organic compound coatings, i.e., cutting off the use of solvents during processing, formulation and application of coatings.
- (iv) Another fruitful approach is the preparation of self-cured 'smart' vegetable oil coatings such as using copolymers. The approach provides a wider platform for potential use of semi-drying or non-drying vegetable oil in coatings as paints.

Genetic transformation of oilseeds may be carried out to improve vegetable oil productivity to yield vegetable oil with desirable fatty acid composition and to improve the performance of vegetable oil derived polymers for use in coatings.

6. Conclusion

Vegetable oil is triglyceride of higher molecular weight fatty acids and most of the vegetable oils have high content of unsaturated fatty acids, which can be converted into epoxy fatty acids. Epoxidized vegetable oils are nowadays gaining importance because of their sustainable, renewable and environment friendly nature. They are widely used as feedstock for the synthesis of plasticizers, lubricants, coating formulations, polyols etc. Vegetable oils constitute the single, largest, easily available, low cost, non-toxic, non-depletable, biodegradable family yielding materials that can compete with fossil fuel derived petro-based products. The outstanding feature of vegetable oil is their unique chemical structure with to unsaturation sites, epoxies, hydroxyls, esters and other functional groups along with inherent fluidity characteristics. These enable them to undergo various chemical transformations producing low molecular weight polymeric materials with versatile applications, particularly as chief ingredients in paints and coatings.

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