INDIAN RESINS MANUFACTURERS` ASSOCIATION

eNewsLetter
Edition: JULY 2022

INDIAN RESINS MANUFACTURER'S ASSOCIATION (IRMA)
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Published by

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From The Editor's Desk

Dear Friends,

I am delighted to take over the Editorship of this prestigious IRMA e-Newsletter. This the first issue after the pandemic.

With all of your support and contribution I will make every effort to bring the magazine regularly with good and useful reading material. You are most welcome to give your suggestions to further upgrade IRMA e-Newsletter. We also request you all to give us articles on technical, commercial or any other subject of educate value to our members.

Friends, I have always believed in taking different and interesting responsibilities and fulfil them to the best of abilities. I must express my thanks to the Managing Committee for giving me the responsibility of Editorship of Irma e-Newsletter.

Since the situation is improving IRMA plans to organise Workshops/Seminar/Interactive meeting etc., for the benefit of all Members. We request all members to whole-heartedly support and participate in the events.

HAPPY READING!

N. Kannan
Chief Editor

From The President's Desk

S. Mahadevan
President

Greetings from IRMA!

It's my pleasure to address you for the first time as President of your Asssociation after being elected to this office in September 2021. The past two years has been a period gripped with uncertainty in the wake of Covid. The War between Russia and Ukraine has added fuel to the above grim situation. During this period the global economics have been hit by Supply Chain crisis, Raw material shortages affecting all segments of the industry. The continued spurt in the Global Crude oil rates plays an ideal spoil sport in the above scheme.

As the saying goes "When the going gets tough, the tough gets going". Our industry is resilient enough to weather these passing storms.

I take this opportunity to welcome the young and vibrant team at IRMA and look forward to their support to deliver what we have set our vision on. Also would like to congratulate the Editorial team of IRMA for bring out the 1st edition of IRMA e-Newsletter after a gap of 2 years.

With the Covid fears receding we will be coming out with our much awaited Workshops, Seminar and Interactive forums very soon. With a bountiful monsoon and cooling of Global Crude we expect cheer to all across the industry in days to come. The Indian growth glory has just begun, and together we will.

S. Mahadevan
President

IRMA Managing Committee 2021-22

S. Mahadevan
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Bioresins: The Need of Tomorrow

Devesh Sane

M.Tech Surface Coating (ICT Mumbai) Department of Polymer and Surface Coating

ABSTRACT

The future generation of thermosetting polymers generated from natural resources is discussed in this article for better sustainability in a variety of applications. Due to the depletion of fossil fuels and the need to safeguard the environment from carbon emissions, bio-based polymer products have gained popularity in the last two decades. Here epoxy, acrylic, phenolic, PU, UPR and benzoxazine resins are shortly discussed. The functionalization methodologies are also summarised to further widen their applicability. The goal of this project is to make us more aware of the current state of bio-based thermosetting resins and to encourage their quicker development, particularly in practical applications.

Keywords: benzoxazine resin, bio-based, epoxy resin, thermosetting resin, PU, UPR, Phenolic, acrylic

INTRODUCTION

We are all aware of the world's population's fast rise and improvement in living conditions. Due to the volatility in crude oil prices and availability, as well as to safeguard the living environment, bio-based resins are in high demand (future generation survival).[1] Bio-based products are being developed and used as an efficient strategy to conserve petroleum resources and maintain our living environment. Until date, considerable amounts of bio-based thermoplastics including poly(lactic acid), polyhydroxyalkanoates, and poly(butylene succinate) have been successfully manufactured and marketed. However, compared to the tremendous advances seen in bio-based thermoplastics, bio-based thermosetting resins have received far less attention.[11] In recent years, research has focused on developing bio-based thermosetting resins from natural oils, cardanol, wood/lignin, itaconic acid, tannins, sugars, lactic acid, and other renewable resource materials to contribute to the polymer industry's sustainable development. The use, efficient chemical transformations, and advantages of bio-based materials, on the other hand, demand a lot of attention. As a result, bio-based polymers have a significant role to play in the green chemical sector.[1] This article aims to briefly cover the advances in the bio based raw materials and some synthesis of mainly epoxy, acrylic, phenolic, UPR, PU and benzoxazine resins.

ACRYLIC RESINS

In the last few years, a large number of molecules have been studied for the production of acrylic resins. Bio acrylates have been produced from phenolic compounds derived from lignin. They are obtained through oxidative coupling of phenolic compounds. The presence of this phenolic functionalities after deprotonation act as a nucleophile and they can offer esterification possibilities to synthesis acrylates.[2] Another sort of natural chemical that can be exploited to make novel acrylate monomers and polymers is terpenes and terpenoids. The four most available terpenes : (+)-α-pinene, (−)-β-pinene, (R)-(+)-limonene, and (R)-(−)-carvone are widely used by modifying their chemical structures by adding acrylate and methacrylate groups. The various terpene based acrylate monomers have been illustrated below in Fig 1[3] It was also proposed to use methanol in place of terpenes although there have been a few attempts to make menthol-based acrylate by esterifying acrylic acid, the yields have been low to moderate, most likely due to the decreased reactivity of a secondary alcohol in comparison to primary alcohol. [2] Lactic acid which is one of the most popular bio-synthons can also be used by esterification to produce acrylates. Isosorbide is also gaining popularity and not lately in 2012 a group of researchers proposed a 5 step method for synthesis of isosorbide based acrylates and produced an yield of 23%.[4]. Many other compounds such as lactones, glycerol, levoglucosenone, fatty acids and many more have also been studied.

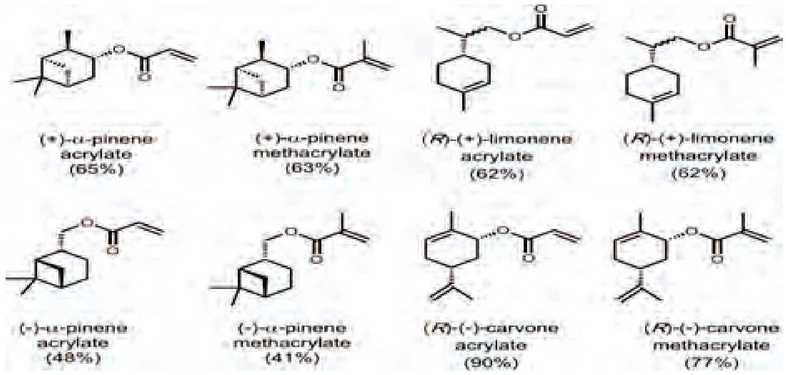


Fig.1 Terpene based acrylate monomers [2]

In majority there are two methods used for preparation and then polymerization of acrylic monomers.1) α-methylenation of esters or lactones. 2) esterification of the hydroxyl moiety, commonly called acrylation or methacrylation. Because of its simplicity, esterification of alcohol to produce new acrylates is now the most popular approach. Originally carried out using acryloyl species in a halogenated solvent, numerous improvements have been reported, including the use of acrylic anhydride. Furthermore, a few compounds have been converted to acrylates using greener methods that do not use traditional acrylation conditions or α-methylenation.

PHENOLIC RESINS

The wide range of properties of phenolic resins such as excellent mechanical properties, flame retardancy, flexibility, low cost, high thermal stability, and water and chemical resistance make them dominate the resin market even after 100 years of its synthesis.[5] Lignin based phenolic resins have been thoroughly studied and the large amount of hydroxyl groups present on them make them suitable for reaction with formaldehyde but in terms of practicality the presence of methoxy group and the steric hinderance are the main issues.[6] Lignin is normally used in three types raw, purified and chemically modified. The raw one has low reactivity and hence a low rate of substitution and hence mainly the purified one is preferred. Chemical modifications such as methylation, phenolation and demethylation are three main techniques used.[5]

opening reactions are among the several ways for the manufacture of vegetable-oil-based polyols that have been documented and shown below. Epoxidation and then interaction of the epoxy groups with various ring-opening reagents such as water, alcohol, glycerol, 1,2-propanodiol, and acids are the main reaction routes for the production of polyols.[9] CNSL has been used as a binder for a number of applications from several years in addition to vegetable oil. High vacuum distillation of CNSL yields cardanol, a key precursor for many oligomers and polymers. To generate autoxidizable bio-based polyurethane with isocyanates, cardanol is significantly changed (phenolic hydroxyl group is the most frequent modification site). A 15-carbon side chain is present in all cardanol-based polyols at meta position, which may alter the thermal and mechanical characteristics of polymers. Cardanol-based polyols are made by altering the unsaturation sites on the 15-carbon side chain. [10]

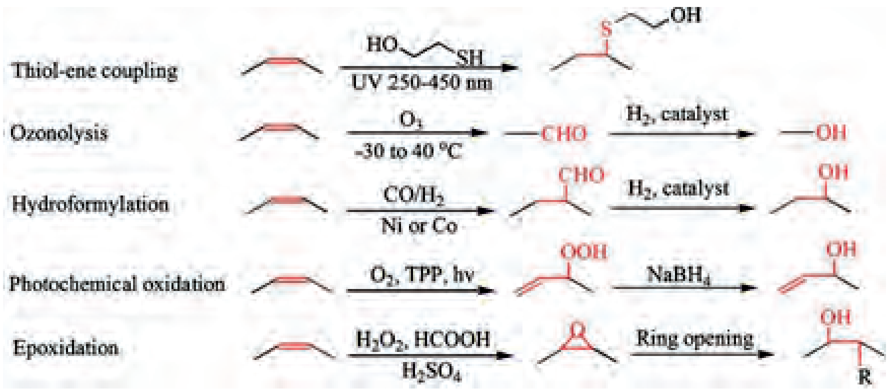
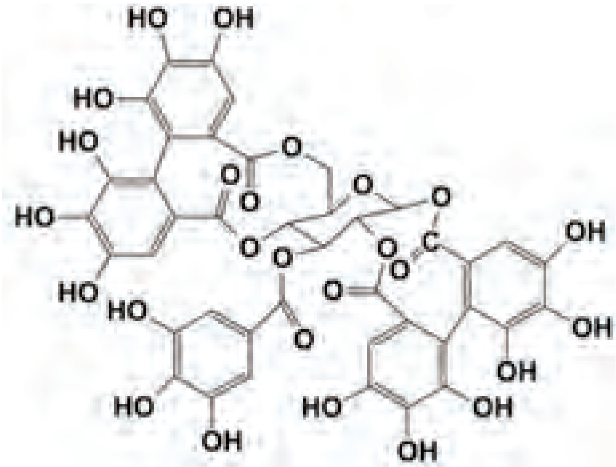


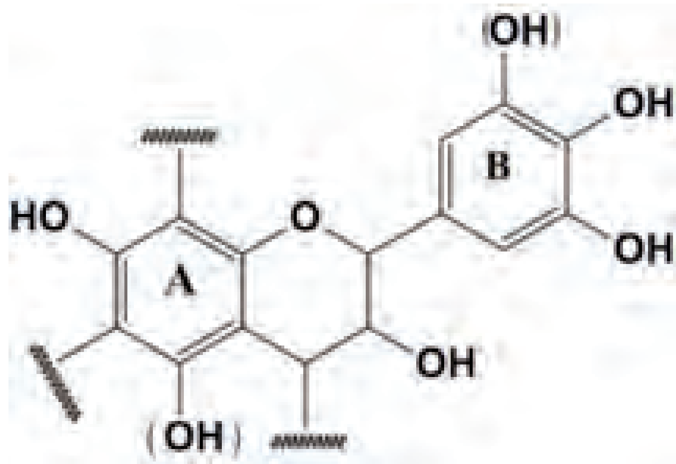
Fig 3. Synthesis of vegetable oil based polyol [10]

Furthermore, tannin-furfuryl alcohol is a natural ingredient that is used in the industry to create hard polyurethane foam phenolic blends by reacting with isocyanate polymer. The primary components utilised in their synthesis are isocyanates, but they have one important drawback: toxicity. Chemical synthesis pathways for nonisocyanate polyurethanes (NIPUs) have been established as a result of this. Tannins are made up of aromatic and aliphatic hydroxyl groups in phenylpropane units. The aromatic hydroxyl group is connected to the unsaturated carbon (sp2) in the benzene ring, which is the benzene ring that can resonate to stabilise the phenoxide ion's negative charge, whereas the aliphatic hydroxyl group is tied to a chain on the saturated carbon (sp3). In the process of manufacturing isocyanate-free polyurethanes, these discrepancies might lead to interbehavioral activities.[7]

UNSATURATED POLYESTERS

Bio-based diacids and diols with unsaturated bonds have typically been used to make bio-based UPEs in recent years. Itaconic acid shares the same chemical structure as maleic acid, with two carboxyl groups and one carbon–carbon double bond. Itaconic acid has therefore been utilised to synthesis bio-based UPEs as a viable alternative to maleic acid and maleic anhydride. Reactive carbon–carbon double bonds were inserted into the main chain of poly(butylene-succinate) prepolymers by the condensation process between 1,4-butanediol, succinic acid, and itaconic acid or maleic acid.[11] Isosorbide and its analogues are also favored due to its rigid di-heterocyclic structure. The rigidity and ability to initiate a Diels-Alder reaction also makes furan based materials an potential starting material but the colour of the product obtained in of concern.[12]





(a) (b)

Fig 2. Structures of (a) hydrolysable tannins and (b) condensed (flavonoid) tannins.[5]

Tannin, a polyphenolic biomolecule found in tree bark and wood, is another major green replacement for phenol in PF resin manufacturing. Tannins are divided into two types based on their chemical properties: hydrolysable and condensable tannins. By treating them with mild acids and bases, hydrolyzable tannins include a combination of phenols, which may be hydrolyzed into phenolic acid, and carbohydrates. Condensable tannins have a simpler structure and are less reactive than hydrolysable tannins. Hydrolysable tannins are utilised to replace phenol in PF resin

despite their reduced reactivity. Condensable tannins, which have two aromatic rings with distinct hydroxyl groups, account for over 90% of commercial tannins. Condensable tannins are more widely employed in resin synthesis than hydrolysable tannins because of their increased reactivity.[7] Cardanol has been employed as a natural alternative for phenol in the manufacturing of PF resin due to the presence of phenolic groups on it. With the partial replacement of cardanol for phenol, both novolac and resol resins have been produced. Formaldehyde which the other main component of phenolic resin despite the fact that formaldehyde is a critical resource in the sector, its negative effects on human health have prompted industry and researchers to seek for safer, more ecologically friendly alternatives. The most major formaldehyde replacement option would be bio-based alternatives. Finding a replacement with strong reactivity and low molecular weight is the most difficult part of replacing formaldehyde. In the synthesis of phenolic resin, hydroxymethylfurfural (HMF), furfural, terephthalaldehyde, and glyoxal have all been described as suitable formaldehyde substitutes.[5]

POLYURETHANE

Bio-based polyurethane (PU) have replaced petrochemical-based coatings in recent decades due to their lower environmental impact, ease of supply, cheap cost, and biodegradability. Vegetable oils, cardanol, and tannins are examples of bio-derived materials. Castor, soybean, sunflower, olive, peanut, canola, corn, and safflower oil derivatives, among others, are utilised as naturally acquired bioresources to make a wide range of biobased polyurethanes with various structures and chemical compositions.[8] The thiol-ene coupling reaction, ozonolysis, hydroformylation, photochemical oxidation, and epoxidation followed by ring

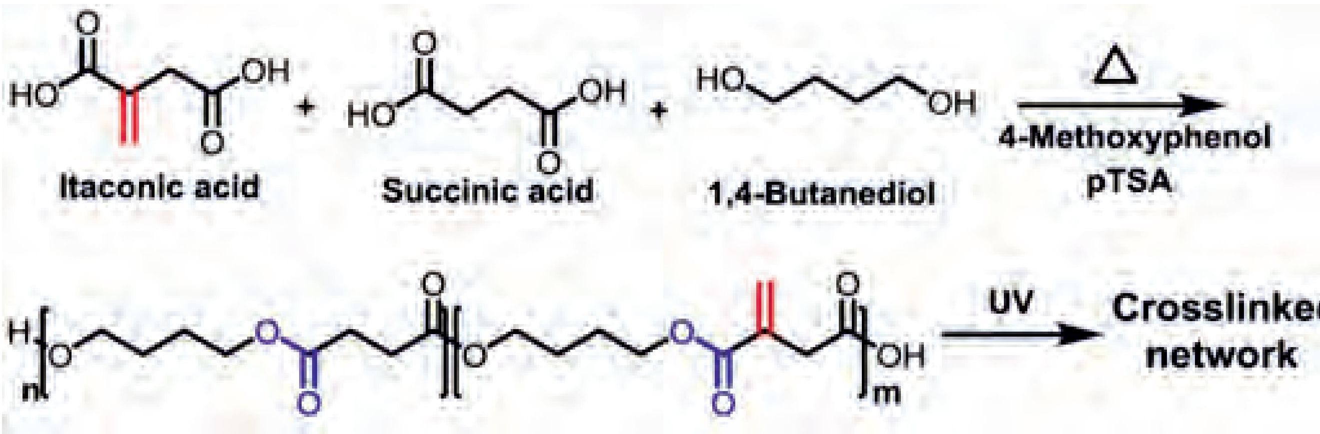


Fig 4. The itaconic acid-based UPs derived from dicarboxylic acid esters [12]

Adjusting the feeding ratio or copolymerization are the most often utilised ways for controlling characteristics in existing research, and employing polyols for branching such as xylitol and pentaerythritol has also proven to be an effective strategy. The petroleum-based phthalic acid, isophthalic acid, and other similar acids are still difficult to replace due to the lack of rigid groups and the lack of renewable building blocks containing diol or diacids and aromatic rings. However, simultaneously constructing UPs with high bio-based content and rigid groups in the main chain is still difficult.[12] Furthermore, due to its simple structure and appropriate physical characteristics, styrene remains an important reactive diluent; nonetheless, a few studies have shown that styrene could be partially replaced by biobased polyester polyol obtained from lactic acid and 1,2 propanediol.[13]

EPOXY

The commercial importance of epoxy resin in various sectors and the toxicity of the starting materials, such as Bisphenol A, researchers and industries have shifted their focus to the synthesis of bio-based epoxy resin, which is expected to be derived from renewable natural resources such as vegetable oil, lignin, rosin, furan, sugars, and itaconic acid, which are widely available, inexpensive, and biodegradable.[14] The most effective bio-based substance is vegetable oil. It includes not only intrinsically branched fatty long chains, but also unsaturated double bonds, which provide a reaction site for epoxidation. Castor oil, soybean oil, and linseed oil are the most fascinating and widely used among them.[15] Epoxidized soybean oil (ESO) is a commercially accessible and widely used plant oil-derived epoxy resin that is primarily utilised as a plasticizer and stabiliser for poly(vinyl chloride), pigment dispersion agent and chemical intermediate, as well as in lubricants and cutting fluids.[11] Glycerol is one of the most significant fatty acid downstream products, with the epoxy derivative (glycerol triglycidyl ether) serving as a diluent and adhesive. Similarly, the carbohydrate derivatives sorbitol are typical polyols, and grafting epoxy groups produces epoxidation products.[13] Lignin is a huge and complex natural polymer that is one of the most plentiful renewable resources, second only to cellulose. It has a large number of hydroxyl and phenolic hydroxyl groups, which may be immediately transformed to reactive epoxy groups by reacting with epichlorohydrin.[11] In addition, the utilisation of mono-functional bio-based epoxy resins for diluents to improve processability and flavonoids-derived epoxy resins with inherent flame retardancy have recently provided fresh ideas for developing resins with these abilities.[12]

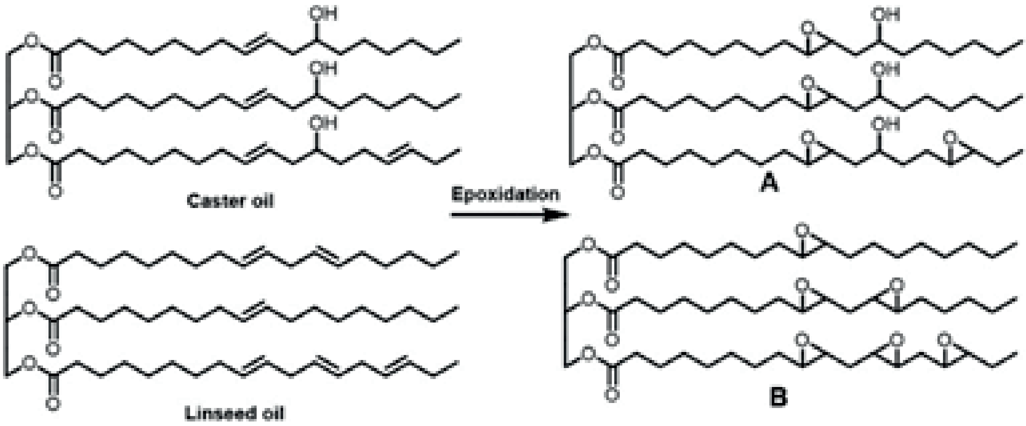


Fig 5. Vegetable oil-based epoxy monomer derived from castor oil and linseed oil [11]

BENZOXAINE

Benzoxazine resins are often made by combining phenols, primary amines, and aldehydes (mostly formaldehyde or paraformaldehyde) in a solvent or solvent-free Mannich condensation procedure.[15] A large number of bio based phenols and amines can be used as raw materials for this resins because of their molecular design flexibility. Mostly phenols are used to produced resins with versatile properties such as flame retardancy and high Tg as phenols in comparison to amines have more species and manoeuvrability.[12] An example is daidzein which gives the resin a unique benzopyranone structure, which gives it anti-bacterial as well as flame retardant feature. Furfurylamine is an intriguing and crucial amine feedstock for bio-based benzoxazine resin production ,benzoxazine's distinctive furan ring gives it unique features. Several research groups created benzoxazine monomer by combining different monophenols such as eugenol, vanillin, guaiacol, arbutin, sesamol, and phloretic acid with furfurylamine .[15] Furthermore, the recent advancements in amino acids are worth noting. Furthermore, the recent invention of bio-based aldehydes allows for the production of strictly totally biobased benzoxazine. In addition, the development of multi-functional resin materials and more environmentally friendly processes will be the trend of bio-based benzoxazine with the discovery of microwave-assisted synthesis, solvent- free synthesis, or other preparation approaches.[12]

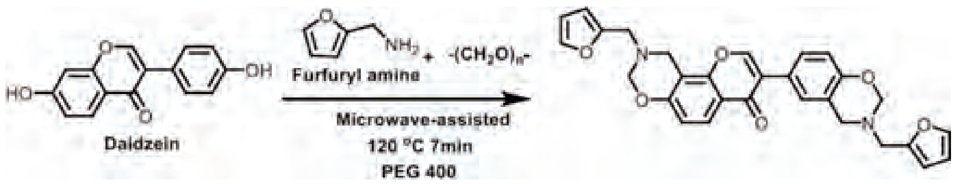


Fig 6. Synthesis of daidzein-based benzoxazine [15]

CONCLUSIONS

Biobased resins have gotten a lot of attention in recent years because they have a huge amount of potential to replace their petroleum-based resins. The realization that the use of fossil based products increases the global warming and the fact that we must start the development of bio based products have fuelled the research. Till date a large amount of bio derived compounds has been used to synthesise resins with properties comparable to their petroleum counter parts. The manufacture and use of some bio-based materials, however, still has drawbacks such as limited durability, toxicity, and recyclability. In the future, nextgeneration bio-based thermosetting resins should follow the green chemistry concept throughout the whole synthesis process to assure excellent performance and versatility. The fact of the matter is that all of the above issues have already received sufficient attention, and significant progress has already been accomplished. Rather than focusing on a bio-based approach, we must keep the goal of establishing a long-term sustainable process in mind.

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EVENTS
AGM held on September 2021

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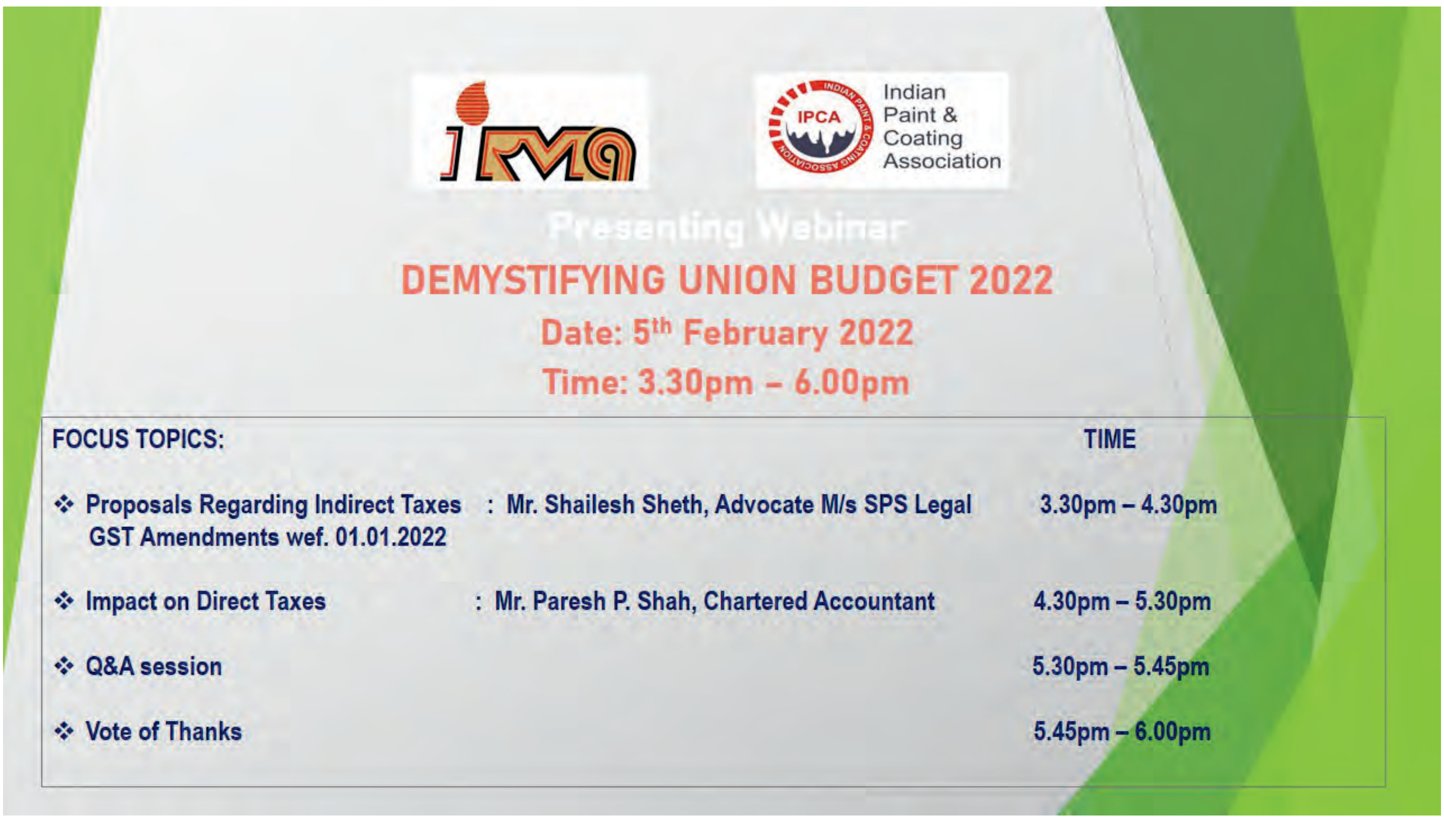
DEMYSTIFYING UNION BUDGET 2022

IRMA with IPCA conducted online meeting on the topic "DEMYSTIFYING UNION BUDGET 2022 on 5th February 2022. Mr. Shailesh Sheth, Advocate M/s.SPS Legal gave a presentation on the Proposals Regarding Indirect Taxes GST Amendments w.e.f. 01-01-2022 and Mr. Paresh P. Shah Chartered Accountant gave a presentation on Impact on Direct Taxes. It was well received by our Members. Irma MC members photo with suit etc.



RAW MATERIAL SCENARIO

Current market rates trend as on10th July.

Soyabean oil	-	137₹/kg (-15₹)
Linseed oil	-	140₹/kg (-5₹)
Commercial castor oil	-	154₹/kg (-2₹)
BPCL MTO	-	Rs 155.58₹/ kg. (+13.02₹)
Reliance slop OIL PX	-	105₹/ kg (+13₹)
Mix. Xylene reliance	-	105 ₹/ kg (-10₹)
Glycerin	-	120 ₹/Kg (-18₹)
Phthalic anhydride	-	115₹/kg (-3₹)
Fatty acids	-	124₹/ kg (-6₹)
Gum Rosin	-	132₹/kg imported grade (-5₹) 125₹/kg Nepal grade (-5₹)
Maleic anhydride	-	125₹/kg. (-15₹)
Ethyl acetate is	-	104₹/ kg
Butanol.	-	143₹/kg

- Compiled by Hiren Shah