International Journal of Pharmaceutical Research and Applications
Volume 6, Issue 3 May - June 2021, pp: 1096-1108 www.ijprajournal.com ISSN: 2249-7781

Use of D- Limonene as an Alternative to Acetone in Nail Polish Remover

Kanchan Kuralkar[1], Kalyani Thakre[1], Harshali Chonde[1], Divya Atram[1], Pratiksha Deulkar[1], Dr. Mitali Bodhankar[1]

[1]*Department of Pharmaceuticals Science, Gurunanak College of Pharmacy, Maharashtra, Nagpur, India 440004*

Corresponding Author: Kanchan Kuralkar

Date Of Submission: 01-06-2021 Date Of Acceptance: 17-06-2021

ABSTRACT

Nail polish remover are organic solvents that break down and dissolve the polish ,thus removes it from nail plate. Nail polish remover generally contain acetone which is very harmful to skin, such as drying out nails, leaving white residues on nails, it strips off nails, their oil and dries them out, nails become brittle and prone to peeling and splitting, therefore the development of alternative to acetone in nail polish remover is necessary.

D-limonene is a chemical found in the rind of citrus fruits such as lemons, limes, and orange. It is widely used in many cleaning product. It helps to loosen/dissolve grease, fat/organic material. It is naturally occurring and biodegradable solvent and is non-toxic unlike acetone and friendly with the nails, so it can be a great replacement of acetone in nail polish remover. The current review emphasizes on the cleaning property of the d-limonene.

KEYWORDS: Acetone, D-limonene, Nail polish, Nail polish remover

I. INTRODUCTION

Nail polish remover is often an organic solvent with added scents and colors, the classic and most recognize remover is acetone. More recently acetone free liquid has been commercialized which largely consist of gamma Butyrolactone [GBL](1). Ethyl acetate may be another organic solvent use for removing nail polish (2).Nail polish remover may come in different preparation : from bottled liquid requiring cotton ball or pads for application, to Pre-submerged pads, to liquid infused into a foam in which one insert their finger to clean their nails. The major health risk associated with nail polish and nail glue removal seems to be due to ingestion of the substances. Ingestion of acetone may cause lethargy, confusion, and decrease arousability for several hours (3).Consumption of chemical such as acetone and GBL may lead to a worrisome clinical presentation initially, with vomiting, coma, and Cardiorespiratory demise (1, 4).

D-Limonene has been produced since 1995 and has been used as a flavor and fragrance additive in cleaning and cosmetic products, food, beverages, and pharmaceuticals. It is also increasingly used as a solvent (5). The dextrorotatory isomer(+)-limonene (or d-limonene) is the principle component of the essential oils present in the rind of citrus fruits, such as orange, lemon, mandarin, grapefruit and lime (6). D-limonene has an outstanding balance of properties including easy removal of coatings (finger nail polish) on hard surfaces, being non-irritating, having a pleasant odor, being quick drying, having miscible ingredients, and leaving the cleaned surfaces free of surface fiber. The d-limonene helps to loosen or dissolve grease fat or organic materials. D-limonene has an outstanding balance of properties including easy removal of coatings (finger nail polish) on hard surfaces, being non-irritating, having a pleasant odor, being quick drying, having miscible ingredients, and leaving the cleaned surfaces free of surface fiber and is less toxic to human in comparison with acetone (7).

Nail polish

Nail polish, also called nail enamel or nail varnish, is a viscous lacquer that is applied on the surface of nail plate of fingernails and toenails to form a water-resistant coating, primarily for cosmetic enhancement (8). It is one of the most widely used cosmetics throughout the world and it was estimated that in 2011, US consumers spent around 6.6 billion dollars only for nail enhancement (9).

International Journal of Pharmaceutical Research and Applications
Volume 6, Issue 3 May - June 2021, pp: 1096-1108 www.ijprajournal.com ISSN: 2249-7781

The use of nail polishes can be traced back to 3000 B.C. when the Chinese and Egyptian women used an "herbal-concoction" made of egg-white, gelatin, beeswax, gum Arabic, and vegetable dyes (like henna or mashed rose) to embellish their nails. Bright colours like red, black, and gold were symbolic of power, superiority, and prosperity and were generally reserved for the elite class, while the commoners were allowed only pale shades.

Michelle Menard is generally credited as the first person to conceptualize nail polish based on automobile paint, and he later founded the company Revlon in 1932. Since then, nail polish formulations have evolved to provide a platform for the variety of nail colours and effects desired by the consumers (10). Although the main purpose of using nail enamel is undoubtedly beautification and grooming, it is also used for camouflaging nail surface textural abnormalities (like pitting, lines, ridges) and discolorations (yellow or white). It is also used to temporarily strengthen thin and brittle nails (11). The basic components include film forming agents, resins, plasticizers, solvents, and colouring agents as summarized in Table-1

Nitrocellulose is the main film-forming agent in nail lacquer, which, along with resins like toluene Sulphonamide formaldehyde, ensures adhesion of the nail paint to the surface of the Nail plate (12). This film is oxygen-permeable, which helps in maintaining the nail health while providing strength and gloss.

Plasticizers like camphor, dibutyl phthalate, or dioctyl phthalate provide flexibility and adhesiveness to the lacquer by linking to polymer chains and increasing the distance between them. Colorants (D&C Red no. 6/7/19) and pearlizers (guanine, bismuth oxychloride, titanium dioxide, ground mica) give the desired colour and shimmer.

Table-1 (15)

Class of constituent	Purpose	Agent
Film-forming agent	When the nail polish is applied the solvent evaporates, leaving the polymer to form a film on the nail	Nitrocellulose, dissolved in solvent, usually ethyl acetate or butyl acetate
Plasticizers	To make sure that nail polish stays flexible when it dries, making the nail polish less prone to chipping	Dibutyl phthalate and camphor, trimethyl pentanyl di-isobutyrate, triphenyl phosphate, ethyl tosylamide, glyceryl tribenzoate
Adhesive polymer resins	To ensure that the nitrocellulose adheres to the nail plate's surface	Tosylamide-formaldehyde resin, polyester resin or cellulose acetate butyrate in hypoallergenic nail polishes
Dyes and pigments	To impart color	Chromium oxide greens, Chromium hydroxide, ferric ferrocyanide, stannic oxide, iron oxide, carmine, ultramarine and manganese violet
Opalescent pigments	To add glittery/shimmer look	Mica, bismuth oxychloride, natural pearls, and Aluminum powder
Thickening agents	To maintain the sparkling particles in suspension while the bottle	Stearalkonium hectorite
Ultraviolet stabilizers	Resist color changes when the dry film is exposed to sunlight	Benzophenone-1

All these ingredients are dissolved or suspended in a solvent, such as butyl acetate or ethyl acetate, which evaporate to leave behind the colourful finish (13). The most common side-effects include allergic contact dermatitis (ACD) and nail-plate staining. The most commonly identified allergen is tosylamide formaldehyde resin (TSFR), which is implicated in around 6.6% of the patch test-positive users (14).

International Journal of Pharmaceutical Research and Applications
Volume 6, Issue 3 May - June 2021, pp: 1096-1108 www.ijprajournal.com ISSN: 2249-7781

Table 2 -**Adverse reactions (15)**

Adverse reaction	Explanation / Mechanism	Precaution & management
Brittle nail	Dehydration due to solvent exposure, used in removing nail polish, gel nails	Avoid harsh chemicals. Do not use nail polish remover frequently
Allergic contact dermatitis	Acrylates, formaldehyde, TSFR in Nail polish	Use hypoallergenic formaldehyde-free nail polish
Onycholysis	Excessive use of Nail cosmetics	Rest to nails every 3 months
Yellow staining		Scraping with scalpel
Keratin granulation	Dehydration of nail plate, leading to clumping of keratin protein	Several weeks - long break from nail polish, nail polish remover and chemical in conjunction with using moisturizers and /or hand creams to replenish

NAIL POLISH REMOVER

Nail polish removers are organic solvents that break down and dissolve the polish, thus removing it from the nail plate. These products are also called nail cleansers (15). They are totally different from other cleansers, such as hair, skin and teeth cleansers, as nail cleansers are required to remove only nail lacquers whereas others are used to remove greasy materials, dirt, dust, etc. As nail cleansers are required to be applied on a smooth and highly resistant surface, composition can be different. These preparations rarely come in contact with the surrounding skin, which is not so in the case of other cleansers. So, the chance of damage is much less than shampoos or other cleansers.

Basically, all lacquer removers should contain solvent or mixture of solvents which can dissolve the nail lacquer.

An ideal lacquer remover should have the following characteristics-

1. It should not be too volatile to evaporate during application.
2. It should not be non-irritating to surrounding skin.
3. It should not leave nails fatty or sticky.
4.It should not have strong degreasing effect to leave nails brittle.
5.It should not have unpleasant and obtrusive odour.

Normally the products contain suitable solvent like acetone, ethyl acetate, amyl acetate, ethyl butyrate or mixture of them or toluene along with some fatting agents to compensate the degreasing effect and not to leave the nail brittle. The products are made more attractive by incorporating perfume. Though acetone has an unpleasant odour and strong degreasing odour, still it is widely used due to its good solvent characteristics.

Other solvents, mentioned above, also have some unpleasant odour. Esters of dibasic acids such as dibutyl phthalate, dioctyl adipate are frequently used as they are odourless or have very faint odour. Liquid esters of' higher acids like butyl stearates, isopropyl myristate are also preferred as they are less volatile and odourless.

Further substances used as solvent are butyl, propyl, amyl alcohols, monoalkyl ethers of dihydric alcohols like methyl and ethyl ethers of ethylene glycol and monoethyl ether of diethylene glycol. They are odourless and less volatile. Another good solvent which is suggested by several workers is gamma valrelactone. Fatting agents used to prevent too much drying effect are vegetable, oils like castor oil, lanolin and its derivatives, fatty alcohols etc. To overcome the unpleasant odour of solvents 3-10% of inexpensive floral volatile fragrance can be incorporated. Examples are orange oil, terpene, terpineol etc. (16).

International Journal of Pharmaceutical Research and Applications
Volume 6, Issue 3 May - June 2021, pp: 1096-1108 www.ijprajournal.com ISSN: 2249-7781

Ingredients(16)

Butyl stearate	**3gm**
Ethyl acetate	**20gm**
Butyl acetate	**20gm**
Acetone	**25gm**
Toluene	**32gm**
Perfume	**q.s.**

Prepared by Simple solution.

EVALUATION OF NAIL POLISH REMOVER (16) :-

Like any other products, the tests for identity of the ingredients and their individual quantity, checking of colour shade are part of the quality tests. Apart from these, several other tests are required to be done on the performance and nature of the products and film produced. Sometimes the product is evaluated against a standard or established product.

1) **Non-volatile content**: This can be done by taking a definite amount of lacquers and applying on a plate of flat surface. Weight of the residual film after evaporation of solvent will indicate the non- volatile content.
2) **Drying rate**: This can be done by taking the product on a flat surface and touching the product with tip of finger at short intervals of time to feel the tackiness. Time taken for disappearance of tackiness is noted.
3) **Smoothness**: This is the character of the film. The film is applied on a surface and the surface characteristics of the film are studied microscopically.
4) **Hardness**: This is the measure of the hardness of film. After application of the film on a flat surface the hardness in measured by applying pressure mechanically.
5) **Adhesion**: This is the measurement of adhesion character of the film with adhering surface. This is done by applying the film and then measuring the adhesion character by trying to remove the film mechanically and the force required for that.
6) **Abrasion resistance**: This quality is studied by applying the film on a surface and then a mechanical abrasive effect is applied. The surface characteristics of the film are studied before and after abrasive effect.
7) **Water resistance**: This is the measurement of the resistance towards water permeability of the film. This is done by applying a continuous film on a surface and immersing it in water. The weights before and after immersion are noted and increase in weight, is calculated. Higher the increase in weight lowers the water resistance
8) **Viscosity**: This is also an important character and can be measured by any viscometer. It can simply be measured by the flow of lacquers from the applicator brush and comparing it with a standard or good commercial product.
9) **Stability**: Stability study of the product as well as colour is also very important and essential. This can be done by accelerated stability test (16).

DISADVANTAGES OF ACETONE (In nail polish removers):-

- The use of acetone is disadvantageous as it gives off a disagreeable odor.
- Acetone is irritating to the eyes and skin as well.
- It is also drying to the nails and cuticles.
- Acetone is flammable and combustible and can be harmful to the user (17).
- Drawback of conventional nail polish removers that contain acetone causes corrosive damages (18).
- A problem with this method (acetone containing nail polish removers) is that the skin of the finger is also in direct contact with acetone.
- Prolonged exposure to acetone can damage the skin.

International Journal of Pharmaceutical Research and Applications
Volume 6, Issue 3 May - June 2021, pp: 1096-1108 www.ijprajournal.com ISSN: 2249-7781

- This method also results in acetone contacting the skin, as evidenced by a white appearance of the finger when the foil wraps are removed.
- In some cases, prior to soaking in acetone, an electric nail buffer or drill is used to remove the top layers of nail polish prior to soaking in acetone. This can be damaging to both the nail and surrounding skin (19).
- Acetone penetrates through the skin and is known to be harmful to the liver also (20).

ADVANTAGES OF D-LIMONENE OVER ACETONE: -

- Addition of D-limonene provides an easy-to-make, easy-to-use very efficient nail polish remover composition or an artificial nail remover composition and methods of using the compositions.
- It also provides a very effective and non-toxic nail polish remover.
- It also provides a non-aqueous liquid cleaning composition especially adapted for removing finger nail polish.
- The cleaner composition has an outstanding balance of properties including easy removal of coatings (finger nail polish) on hard surfaces.
- Being non-irritating, having a pleasant order and being quick drying, it is good to use.
- Having miscible ingredients in the composition and leaving the cleaned surfaces free of surface fiber, it seems a effective acetone free nail polish remover (17).

II. MATERIAL &METHODS: -

D-LIMONENE

D-limonene can be found in citrus peels such as orange and lemon peels. A large amount of orange peel waste is discarded annually; however, orange peels contain essential oils, which contain the compound, limonene (21). Limonene is a valuable compound used in food, cosmetic, and pharmaceutical applications (22).

CHEMICAL AND PHYSICAL DATA

Often denoted as "D-limonene" (23) the dextrorotatory isomer (+)-limonene (or d-limonene) is a monocyclic terpene comprising two isoprene units abundantly produced in nature as secondary plant metabolite (24). The isomer is the principle component of the essential oils present in the rind of citrus fruits, such as orange, lemon, mandarin, grapefruit and lime. The other optical isomer, (-)-limonene or l-limonene, has a turpentine smell and is also found in plants as the major component of volatiles emitted by oaks and pines (6).

d-Limonene is a colorless oil sparingly soluble in water (13.8 mg/L at 25°C) with a sweet orange smell, widely used in cosmetic and food industry. Commercially, the terpene is mostly obtained from waste orange peel (dry orange peel waste contains 3.8wt.% of d-limonene on a dry weight basis) (25).

METHOD OF EXTRACTION

The orange peel which is considered as a waste can be used for the extraction of limonene (D-Limonene) which has many applications ranging from food flavouring agent to cosmetics. Limonene can be extracted by various conventional methods like:

- Steam Distillation
- Cold Press,
- Solvent Extraction,
- Super Critical CO_2 Extraction,
- Solvent Free Microwave Extraction.

It means varied typical ways like steam distillation cold press, solvent extraction, novel ways like super essential greenhouse emission extraction. The conventional method though simple are robust and the yield percentage is less whereas the novel methods are not cost effective as well as easy the yield share is a smaller amount whereas the novel ways aren't price effective (26).

1. **Steam distillation** (26)

The orange peels were cut into small size and were pre heated below 100 degree Celsius at constant temperature at 30, 60,90 and 120 minutes respectively for 4 readings.

It has been observed that yield of the D-limonene increases with increasing time. Steam distillation is the promising method for the extraction of D-limonene. The increase in orange oil d-limonene yield (%) by steam distillation is more due to reasons that the orange peels were pre heated Which softened the cell walls of the orange peels which are made up of cellulose, hemicelluloses and pectin and the orange peels were pre heated that softened the cell walls of the orange peels that square Measure created of polysaccharide, hemicelluloses and cellulose. Once the pre heated peels were additional subjected to traditional steam distillation procedure, it additional softened and open the cell walls of the

International Journal of Pharmaceutical Research and Applications
Volume 6, Issue 3 May - June 2021, pp: 1096-1108 www.ijprajournal.com ISSN: 2249-7781

orange peels to liberate all the parts gift in it within the variety of orange oil (26).

2. Cold Pressing

The Cold Press, one of the ancient essential oil extraction methods and already integrated in most of the modern juice production systems, is based on the use of needles to tear the oil glands in the peels (27,28) and the use of a mechanical pressure to release the Oils (29), has the major advantage of minimizing the degradationof the essential oil constituents (30), being the oil expeller-pressed at low temperature and pressure. Additionally, the resulting oil is 100% pure and retains most of the volatile compounds and waxes, which are important for their aromatic properties (31).

3. Solvent Extraction (32)

Material: -Oranges, Ethanol, Methanol, n-hexane, 1 – Propanol were reagent grade chemicals and used without further purification, Distilled water.

Extraction of D-Limonene: -

Orange peels were separated from the orange by means of a sharp blade and knife. Then cut into small pieces. 100,110,120 and 130 gms of the extracted peels were put in a 500 mL RBF along with 150 mL of ethanol, methanol, 1-propanol, n-hexane and distilled water and heated up to their boiling point under Soxhlation for 4,5,6 and 7 hrs. Then the collected volume fractions of the extraction were fractionally distillated in rotary evaporator to separate the essential oil D-Limonene and the solvents. The pure D-Limonene extracted with various solvents were labelled in vials and kept for further analysis (32).

4. Solvent-free Microwave

There are several methods in which limonene may be extracted. Among the common methods used is, solvent-assisted extraction techniques which often include n-hexane (33). n-hexane is a petroleum-based solvent that is commonly used. However, the use of petroleum-based solvents have disadvantages which include, high energy and time consumption, lower product yield, and hazardous by-products (34). The use of green solvents, which are produced from biomass feedstock, for the extraction of limonene offer a way to improve resource efficiency while also offering hexane replacements (35). However, as an alternative to both of these methods, solvent-free microwave (SMF) assisted technique which will be examined.

A household microwave was perforated at the top, and an inlet pipe was connected to a conical flask (reactor) placed inside the microwave while the other end (outlet pipe) was connected to a condenser. Connected to the condenser was a pipe that conveyed the hydrosol to a reagent bottle. The reagent bottle was used to further separate the contents into water and oil. About 150g of orange and lemon peels were placed into different 100 mL round bottle flasks with no solvent added. Each flask was placed in microwave in 1000 W power output with an adjustable value of 200 W intervals (34).

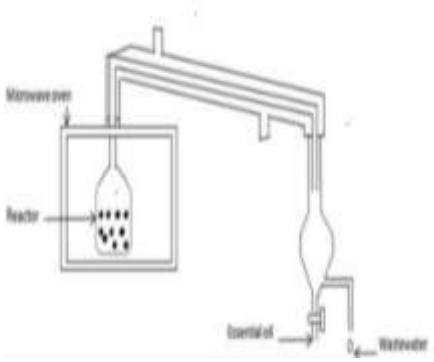

Figure1:A visual of the modified microwave used for the extraction (34).

PREPARATION OF D-LIMONENE BASED NAIL POLISH REMOVER (36)

Composition of d-limonene based Nail polish remover includes: -

1. D-limonene

International Journal of Pharmaceutical Research and Applications
Volume 6, Issue 3 May - June 2021, pp: 1096-1108 www.ijprajournal.com ISSN: 2249-7781

2. Ethyl lactate
3. Cetyl acetate or mixture of Cetyl acetate and acetylated lanolin
4. Optionally, Propylene glycol methyl ether acetate

Advantages Of Each Ingredients (36):-
D-limonene:
• It helps to loosen/dissolve grease, fat/organic material.
• It is described as a cleaner in U.S. Patent nos. 4,790,951 and 5,031,648

Ethyl lactate

- As indicated, relatively large amounts of ethyl lactate can be used, say, about 10 to 20 up to 50 or 70% by weight. Preferably about 30 to 55 weight percent is used to obtain fast drying.
- Ethyl lactate is a solvent that is compatible with d-limonene, cetyl acetate, Acetulan (mixture of cetyl acetate and acetylated lanolin alcohol), and the optional ingredient (propylene glycol methyl ether acetate).
- Ethyl lactate enhances the compatibility, efficiency, miscibility, and the stability of the liquid, the speed of drying the non-aqueous d-limonene/acetulan combination and enhances the removal time for the more difficult hard nail polish surfaces.
- Best results are obtained with about 40-50% by weight.
- As indicated, the total amount of d-limonene in the composition is preferably at least 20 or 30 percent by weight and more preferably at least about 27 or 45 percent by weight.
- In some cases, methyl lactate can be used with the ethyl lactate, the methyl lactate being generally about 3 to 5 weight percent up to 50 to 55 weight percent of the combination of ethyl lactate and methyl lactate.

Cetyl acetate
• It is a desensitizer that enhance the compatibility, efficiency, miscibility & stability of liquid non-aqueous d-limonene combination.
• It gives best result at 2-6% by weight in formulation composition. It can be replaced with acetulan.

Acetulan:
• It is a combination of cetyl acetate and acetylated lanolin alcohol in place of cetyl alcohol or with cetyl acetate

FORMULATION: -
An effective, non-toxic, non-aqueous liquid finger nail cleaner composition comprising the following ingredients in the general and preferred ranges set forth in approximate percent by weight:

Ingredients	% By weight (general)	Preferred	Ideal
D-limonene	20-70	30-60	45
Ethyl lactate	20-75	25-55	50
Cetyl acetate	9-17	12-15	5

Optionally, propylene glycol methyl ether can be used as well as a surfactant. These formulations are as follows in approximate % by weight:

Ingredient	Optimal	General
D-limonene	27	15-50
Ethyl lactate	35	10-50
Propylene glycol methyl ether acetate	35	10-50
Acetulan	2	1-50
Surfactant (ethoxylated undecyl alcohol)	1	0.5-5

A fingernail polish remover non-aqueous composition comprising the following ingredients:

Ingredients	% by weight
D-limonene	30-60
Ethyl lactate	25-45
Cetyl acetate	2-7

International Journal of Pharmaceutical Research and Applications
Volume 6, Issue 3 May - June 2021, pp: 1096-1108 www.ijprajournal.com ISSN: 2249-7781

The easy to use, easy to make cleaning composition is made by mixing generally 3 ingredients (d-limonene, ethyl lactate & acetulan) to form Homogenized stable cleaning mixture.

Also provided is a composition in which the following ingredients are present in approximate percent by weight:

Ingredients	% By weight
D-limonene	30-60
Ethyl lactate	10-50
Cetyl acetate	1-5
Propylene glycol methyl ether acetate	10-50

The cleaner composition has an outstanding balance of properties including easy removal of coating on hard surface, being non-irritating, having pleasant odour, being quick drying, having miscible ingredient in formulation and leaving clean surface free of surface fibre.

The compositions of the present invention, while preferably used as a nail polish remover, on silk line, and fiberglass wraps.

The compositions are useful as all-purpose cleaners and, in particular, hard surface cleaners, blanket washes for us in the printing industry, cleaners for brake linings, silk screens, copier belts, all kinds of metering devices including coin collecting machines, and the cleaning of all types of spraying equipment when used for painting, applying glues, inks, greases, oils, etc (36).

INDUSTRY TRENDS (37)

Dipentene (d-limonene) Market size was more than USD 1.2 billion in 2017 and will witness 4.6% CAGR during the forecast timespan.

Global dipentene market is primarily driven by personal care products and food & beverages business across the globe. The product is used as a flavoring and fragrance additive in both the end-user industries. The citrus aroma of the product makes it a desirable choice for food processing companies. Moreover, the product has found widespread application as an ingredient in various cosmetic formulations and personal hygiene care products. Limonene market will substantially grow as a green solvent replacing petroleum-based solvents in industrial and paints & coatings applications in the coming years owing to its bio-degradability and low VOC emission. The market has immense potential to be explored as alternative to mainstream pesticides, owing to its versatile characteristics.

Dipentene has low level of toxicity according to the U.S. EPA. The risk of health effects following repeated limonene exposure is likely to be high during end use of the product in confined spaces and in places with limited ventilation. These factors are likely to hamper dipentene market size growth during the forecast timeframe. Additionally, the possibilities of manufacturing bio-based plastics and polymers with dipentene is being explored by many multi-national companies, which has surged product demand in past few years, ultimately resulting in high product prices for both food as well as technical grade applications.

International Journal of Pharmaceutical Research and Applications
Volume 6, Issue 3 May - June 2021, pp: 1096-1108 www.ijprajournal.com ISSN: 2249-7781

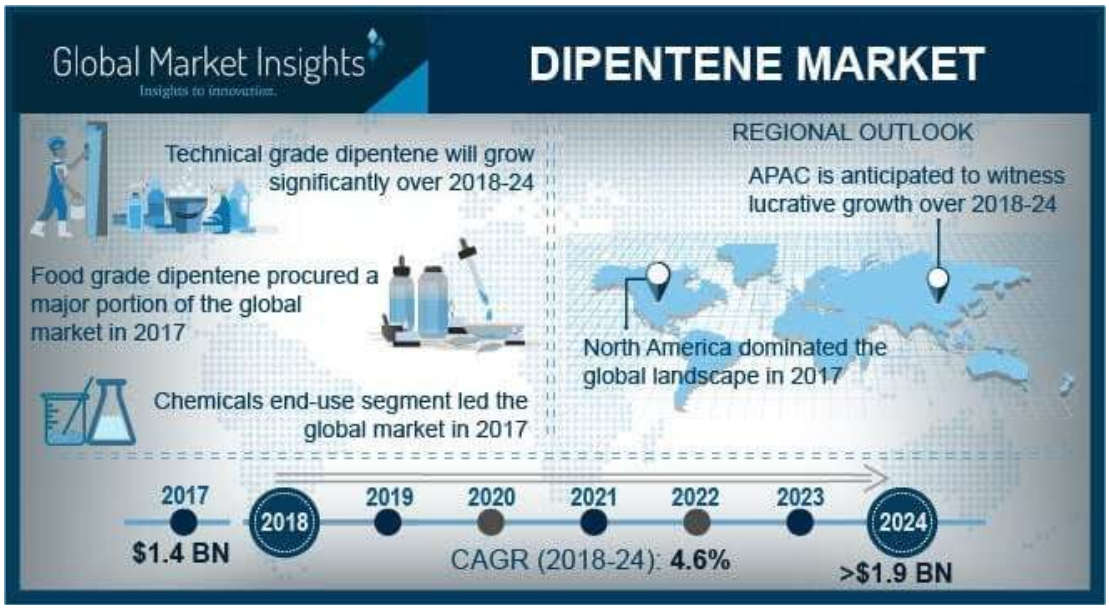

Figure 2: Dipentene Market

➢ Dipentene Market, By Grade

Dipentene is sold across continents in majorly two grades; food and technical. Technical grade is also known as industrial grade in different regions. Technical grade will be the fastest growing segment amongst the two in the coming years. It can be attributed to its application in various end-user industries such as paints & coatings, household cleaning, rubber, chemicals, electronics, etc. The product is increasingly becoming preferred choice in paints industry, where the end-user is marine vessels. General cargo tankers, submarines, ships are drifting towards paints & coatings which are aquatic life friendly. Enamels and lacquers made from petrochemicals emit VOC in water that causes water pollution and poses threat to aquatic animals. Varnishes and paints made from technical grade dipentene will be a green alternative to these conventional paints and help in reducing water pollution.

Food grade held the largest share in global dipentene market in 2017 due to its particular citrus aroma which makes it an active ingredient for essential oils. Food grade dipentene is also used in making various drugs owing to its antioxidant and anti-inflammatory properties. The expansion of hypermarket and supermarket retail format has driven demand for processed food and drinks. Consumers are actively looking for foods that are mostly ready-to-eat and healthy also. This drifting trend has created demand for pool of products which are processed with natural ingredients. This shall create elevated food grade demand for dipentene in the coming years.

➢ Dipentene Market, By End-user

Chemicals accounted for the largest share in global dipentene market in 2017. Dipentene has numerous applications in chemical industries and other manufacturing plants. It includes its use as a chemical intermediated, degreaser, cleaner and solvent. Dipentene can be used as release agent which can be sprayed on asphalt trucks' beds before picking loads for easy unloading.

Paints & coatings application has enormous demand in automotive and construction sector. It is also witnessing rising demand from marine vessels industry. Paints & coatings are necessary to new as well as recycled components/machines or parts. Dipentene is used as a fragrant alternative to turpentine, and also as a paint stripper. Most paint formulations use a combination of solvent carriers to spread the product over a desired area. Generally, dipentene can be used as the carrier as an alternative to other petroleum-based solvents, often with resulting in reduction in volume of solvent used.

➢ Dipentene Market, By Region

North America was the largest region in global dipentene market in terms of volume and value in 2017. U.S. is among the top 10 citrus fruit

International Journal of Pharmaceutical Research and Applications
Volume 6, Issue 3 May - June 2021, pp: 1096-1108 www.ijprajournal.com ISSN: 2249-7781

producers in the world; hence a large volume of fruits is processed to yield limonene and other fruit oils which are used in various personal care products. Dipentene is widely used in cosmetics such as moisturizers, sunscreen, skin care creams, lipsticks, etc. and U.S. is home to some chief cosmetic producers in the world. Consumers in the U.S. are more aware about the benefits of natural ingredients in cosmetics and have preferences shifting towards bio-degradable products, which will be a prime driver in propelling product demand in the coming years.

Asia Pacific will grow at substantial rates in the coming years due to rising citrus fruit production in China, India, Indonesia, Malaysia, etc. The dipentene production shall witness significant increase in terms of volume due to increasing production plants of multi-national companies which have planned product penetration in these countries. Sturdy growth of end-user industries of dipentene in Asia Pacific will positively influence product demand during the forecast timeframe.

- Competitive Market Share

The dipentene market is highly competitive with major players holding more than 50% of market share in 2017. The key market share contributors in dipentene industry include Florida Chemical Company, Fujian Green Pine Company Limited, Mangalam Organics Limited, Florachem Corporation and International Flavors & Fragrances Inc. The companies involved in limonene business have mergers & acquisitions as their prime expansion strategy. In addition, switching cost for suppliers is very low in the industry. This makes the market more competitive by decreasing entry barriers for the new entrants. Producers are expanding their manufacturing capacity and majority have their own distribution network.

- Industry Background

Dipentene, which is also known as a limonene is an optically active terpene having a lemon like aroma found in orange, peppermint, lemon and other oils. The product is used as wetting agent in paints & coatings and in resin production. Its formula is C10H16. Limonene is a naturally occurring derivative which is biodegradable and nontoxic in nature. Owing to its less toxicity and environment friendly attributes, it has low threat of substitution. Growing paints & coating industry along with agricultural sector will fuel limonene market expansion at significant growth rate over the forecast period. (37)

- **MARKET INSIGHTS**

The worldwide production of d-limonene in 2013 was estimated to exceed 70,000 tons. On the other hand, the global orange production for 2013/14 is projected to rise 5% from the previous 2012/13 season, to reach 51.8 million metric tons as a result of increased production in Brazil, China and the European Union (EU, Table 3) (38)

Table 3. Orange production in selected countries in 2013/14.Data are in 1,000 metric tons

Country	Production	Country	Production
1.Brazil	17,750	9.Morocco	1000
2.china	7,600	10.vietnam	675
3.United states	6,707	11.Argentina	550
4.European union	6,600	12.Australia	465
5.Mexico	3,900	13.costa Rica	315
6.Egypt	2,570	14.Guatemala	150
7.Turkey	1,700	15.Israel	100
8.South Africa	1,500	16.Others	191

Source: US Department of Agriculture, 2014. Adapted from Ref. 16, with kind permission

Brazil is by far the largest producer, with an output approaching 40% of the world's orange production. To grow oranges and citrus fruits in general, hot, humid weather are required conditions because oranges and citrus are susceptible to the cold.

Manufacturers of d-limonene are ubiquitous across the globe. Some 300 orange oil distillation plants are installed worldwide, generally supplying customers with technical grade (95% in d-limonene) or food grade (96%) orange oil. A short list of selected suppliers showing such ubiquity includes Cutrale (Brazil), Hangzhou

International Journal of Pharmaceutical Research and Applications
Volume 6, Issue 3 May - June 2021, pp: 1096-1108 www.ijprajournal.com ISSN: 2249-7781

Dayangchem (China), Merck Schuchardt OHG (Germany), Capua 1880 (Italy), Finetech Industry Limited (UK), Tokyo Chemical Industry (Japan), Acros Organics (USA), Frutarom (Israel) and lemon concentrate (Spain). Like with any other agricultural product, the price of d-limonene is intrinsically volatile. For example, in 2011 the price first reached $11/kg, and then, within months, it fell to $3.3/kg, before resuming its ascent. (39) Demand, in any case, has been constantly rising, and so have supply and price. As of mid-2014, the price in the US exceeded $10/kg. A decade ago, manufacturers of industrial cleaning products were paying as low as $0.4/kg.

Alternative Biosolvent

In the early 1950s, indeed, Henry Schulz created in Florida the first large volume markets for d-limonene commercializing the isomer as a versatile solvent alternative to toxic solvents generally obtained from fossil fuel sources (40). Cleaning products for industrial and household purposes originally represented the largest market for d-limonene.

Table 4. Relevant properties of d-limonene and commonly employed organic solvents

Properties	n-hexane	Toluene	Dichloromethane	D-limonene
1.Boiling point	68.7	110.6	40	175.5
2.KB	29	105	1.36	67
3.Density	0.66	0.87	1.32	0.84
4.Toxicity	High	High	High	Absent
5.Environmental impact	High	High	High	Absent

Source: Paint and Coating Testing Manual, 14th edition, Chapter 18; J. V. Koleske (Ed.), American Society for Testing and Materials: Ann Arbor, MI, 1995.

Toxic solvents such as toluene, n-hexane and chlorinated organic solvents can be effectively replaced by environmentally friendly d-limonene in many industrial contexts (Table 4) (41).

III. CONCLUSION

In the traditional method acetone and alcohol are used for removing the nail polish. D-limonene represents an ecological and sustainable solvent ingredient which has additional advantage as cleaning agent and also has the ability to remove stain. It is an extremely effective and relatively safe cleaner and a very good non-toxic solvent from natural origin which can be used as nail paint remover. The formulation comprising d-limonene has an outstanding balance of properties including easy removal of coating of finger nail polishes or paint and being non-irritating, have pleasant odour and leaving the nail surface clean.

As this is a natural extract less toxic that mineral spirit or acetone can be incorporated into the formulation of nail paint remover as an alternative to acetone.

REFERENCES: -

1. Savage, T.;Khan, A.; Loftus,B.G.Acetone-free nail polish remover pads:toxicity in a 9-month old.Arch.Dis.Child.2007,92,371[CrossRef][PubMed]
2. Chevillotte,G.;Ficheux,A.S.;Morisset,T.;Roudot,A.C.Exposure method development for risk assessment to cosmetic products using a standard composition.Food Chem.Toxicol.2014,68,108–116.[CrossRef][PubMed]
3. Ramu,A.;Rosenbaum,J.;Blaschke,T.F.Disposition of acetone following acute acetone intoxication.West.J.Med.1978,129,429–432.[PubMed]
4. Rambourg-Schepens,M.O.;Buffet,M.;Durak,C.;Mathieu-Nolf,M.Gamma butyrolactone poisoning and its similarities to gamma hydroxy butyric acid:Two case reports.Vet.Hum.Toxicol.1997,39,234–235.[PubMed]
5. S. Nikfar, A.F. Behboudi, in Encyclopedia of Toxicology (Third Edition), 2014
6. J. Schween, R. Dlugi, C. Hewitt and P. Foster, Atmos. Environ.1997, 31, 199-215.
7. Vincent.ADotolo, John. R. Schwartz, Jaye Kraus-Mrachak, Dotolo Research Corp, Nail Polish Remover Composition, United State patent US 5346652A, 1994-Sep-13.

International Journal of Pharmaceutical Research and Applications
Volume 6, Issue 3 May - June 2021, pp: 1096-1108 www.ijprajournal.com ISSN: 2249-7781

8. Jefferson J, Rich P. Update in nail cosmetics. Dermatol Ther2012; 25:481-490.
9. Nail polish. Available from: http://en.wikipedia.org/ wiki/Nail polish accessed on October 30, 2017)
10. Draelos ZD. Nail cosmetic issues. Dermatol Clin 2000;18 675-683,
11. Rich P. Nail cosmetics. Dermatol Clin -. 2006,24:393-399
12. Schlossman ML Nail-enamel resins. Cosmetic Techno 1979:1-53.
13. Draelos ZD. Cosmetic treatment of nails. Clin Dermatol 2013,31:573-5
14. B. Rich P, Kwak H. Nail physiology and grooming. In Draelos ZD, Ed. Cosmetic Dermatology Products and Procedures, 1st ed. Hoboken, NJ: Wiley-Blackwell, 2010: pp. 197-205.
15. Chandra S, Das A. The science of nail polish, nail polish remover, and nail moisturizers. Nail Disorders [Internet]. 2019 [cited 6 June 2021];:497-501. Available from: https://www.researchgate.net/publication/330976621_The_science_of_nail_polish_nail_polish_remover_and_nail_moisturizers_A_Comprehensive_Approach
16. B.M Mittal, R. M. Shah, A handbook of cosmetics science, Delhi, Vallabhprakashan. 2000.
17. Vincent A. Dotolo, John R. Schwartz, Jaye Kraus-Marchak (1992). Nail polish remover composition. (United States Patent No. US5346652A). https://patents.google.com/patent/US5346652A/en Application No. = US07/851,738 events
18. Hsien-Wen LIN (2012). Composition of nail polish remover. (Patent No. 20120315231). https://patents.justia.com/patents-by-us-classification/510/118 Application No. = 20120315231
19. Rochelle Rosemarie Mercado, Fiona Lee Reeve (2015). Nail polish remover. (WIPO; PCT Patent No. WO2015135021A1). https://patents.google.com/patent/WO2015135021A1/en Application No. = PCT/AU2015/000138 events
20. Michael Bernstein (1984). Nailpolish remover composition. (United States Patent No. US4735798A). https://patents.google.com/patent/US4735798A/en Application No. = US06/775,635 events
21. Fakayode, Olugbenga Abiola, and Kingsley Emmanuel Abobi. "Optimization of Oil and Pectin Extraction from Orange (Citrus Sinensis) Peels: A Response Surface Approach." Journal of Analytical Science & Technology, vol. 9, no. 1, Sept. 2018, pp. 1-17. EBSCOhost, doi:10.1186/s40543-018-0151-3
22. Gök, Aslı, et al. "Comparison of Lemon Oil Composition after Using Different Extraction Methods." Journal of Essential Oil Research, vol. 27, no. 1, Feb. 2015, pp. 17–22. EBSCOhost, doi:10.1080/10412905.2014.982872
23. E. C. Ressner, Naming Limonene Correctly. Chem. Eng. News 2011, 89 (23), 4
24. J. C. Mann, J. B. Hobbs, D. V. Banthorpe, J. B. Harborne, Natural Products: their Chemistry and Biological Significance, Longman Scientific & Technical, Harlow: UK;pp. 308–309.
25. M. Pourbafrani, G. Forgacs, I. S. Horvath, C. Niklasson, M. Taherzadeh, Bioresour.Technol. 2010, 101, 4246-4250.
26. Mahajan P, Wankhede P, Gulhane O. Extraction Of D- Limonene from Orange Peels. Yavatmal: Global Journal of Engineering Science and Researches; 2017. p. 42-46.
27. Negro, V.; Mancini, G.; Ruggeri, B.; Fino, D. Citrus waste as feedstock for bio-based products recovery: Review on limonene case study and energy valorization. Bioresour. Technol. 2016, 214, 806-815.
28. Mahato, N.; Sinha, M.; Sharma, K.; RakotiKoteswararao, R.; Cho, M.H. Modern Extraction and Purification Techniques for Obtaining High Purity Food-Grade Bioactive Compounds and Value-Added Co-Products from Citrus Wastes. Foods 2019, 8, 523.
29. Teigiserova, D.A.; Ligia Tiruta-Barna, L.; Ahmadi, A.; Hamelin, L.; Thomsen, M. A step closer to circular bioeconomy for citrus peel waste: A review of yields and technologies for sustainable management of essential oils. J. Environ. Manage. 2021, 280, 111832.
30. Karaman, S.; Karasu, S.; Tornuk, F.; Toker, O.S.; Geçgel, Ü.; Sagdic, O.; Ozcan, N.; Gül, O. Recovery potential of cold press byproducts obtained from the edible oil industry: physicochemical, bioactive, and

antimicrobial properties. J. Agric. Food Chem. 2015, 63, 2305-2313.
31. Rassem, H.H.A; Nour, A.H.; Yunus, R.M. Techniques For Extraction of Essential Oils From Plants: A Review. Aust. J. Basic & Appl. Sci. 2016, 10(16), 117-127.
32. Mirdha, K. and Routray, C., 2020. Extraction and characterization of D-limonine oil from orange peels using different solvents. In: 9th ed. MuktShabd journal, p.9.
33. Lopresto, Catia Giovanna, et al. "A Non-Conventional Method to Extract D-Limonene from Waste Lemon Peels and Comparison with Traditional Soxhlet Extraction." Separation & Purification Technology, vol. 137, Nov. 2014, pp. 13–20. EBSCOhost, doi:10.1016/j.seppur.2014.09.015.
34. Auta, M., et al. "Optimization of Citrus Peels D-Limonene Extraction Using Solvent-Free Microwave Green Technology." Chemical Engineering Communications, vol 205,no.6,June2018,pp.789–796.EBSCOhost, doi:10.1080/00986445.2017.1419206.
35. Ozturk, Baranse, et al. "Orange Peel Waste Valorisation through Limonene Extraction Using Bio-Based Solvents." Biochemical Engineering Journal, vol. 151, Nov. 2019, pp. 1-9. EBSCOhost, doi: 10.1016/j.bej.2019.107298.
36. Bayless Ronnie E. NAIL POLISH REMOVER. US; 5372742, 1994. https://patents.google.com/patent/US5372742A/en
37. Pulidindi, K. and Pandey, H., 2018. Dipentene (Limonene) Market Size by Grade (Food Grade, Technical Grade), By End-user (Personal Care, Food & Beverages, Pharmaceutical, Electronics, Chemicals, Paints & Coatings, Rubber, Agriculture), Industry Analysis Report, Regional Outlook, Application Growth Potential, Price Trends, Competitive Market Share & Forecast, 2018 – 2024. [online] Global market insights. Available at: https://www.google.com/amp/s/www.gminsights.com/industry-analysis/dipentene-market/amp [Accessed 6 June 2021].
38. US Department of Agriculture, Citrus: World Markets and Trade, January 2014. http://www.fas.usda.gov/data/citrus-world-markets-and-trade
39. BAC Reports, D-Limonene (CAS 5989-27-5) Market Research Report 2014, May, 2014.
40. Florida Citrus Hall of Fame, "Dr. Henry E. 'Bert' Schulz (1921 - 2009)". See at the URL: http://floridacitrushalloffame.com/index.php/inductees/inductee-name/?ref_cID=89&bID=0&dd_asId=619 (last time accessed, August 5, 2014).
41. T. Toplisek, R. Gustafson, Precision Cleaning 1995, 3, 17-22.