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Methacrylates Use in Nail Enhancements

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Introductory Remarks by MPA

The Methacrylate Producers Association, Inc. (MPA) and its member companies work jointly to address important health, safety and environmental issues involving the basic methacrylate monomer products.[1] MPA has been aware of the use of liquid methacrylate monomers in nail enhancement products for many years and has a long-standing position of not supporting the use of these chemicals in these applications on grounds that they are skin sensitizers and direct contact between the liquid monomer and the nail or skin cannot be completely avoided.[2] Despite this policy, basic methacrylates continue to be used in these products. Growing concerns over adverse health effects in cosmetologists and consumers, combined with the range and complexity of nail products in the marketplace, encouraged MPA to investigate in greater depth the extent of use of the basic methacrylates in these products. Since neither MPA nor its member companies have any involvement in the manufacture or sale of artificial nail enhancement products, MPA commissioned an independent researcher to summarize the information readily available from the internet, existing reviews and publications.

This overview is provided in good faith. The author has made every reasonable effort to ensure that it is correct and up to date as of the date of publication. However, MPA and its member companies did not independently verify the statements in this paper, and cannot warrant the accuracy and completeness of the information in this review. Any person relying on any of the information contained herein shall do so at their own risk. This review is intended for informational purposes only, and the author and MPA disclaim any liability for any reliance on or use of the information provided.

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As of 2018, there were almost 395,600 nail technicians and just over 56,300 individual nail salons in the United States [1]. In 2018, approximately 8.36 billion U.S. dollars were spent on nail salon services in the U.S. [2]. The nail salon industry in the U.S. is comprised of nail care services including manicures, pedicures and false nails (nail enhancements), as well as the sale of nail care products like nail polish and nail care accessories.

Nail enhancements come in a variety of types, each having unique functions. Nail coatings provide a clear or colored finish, which may serve to strengthen or to decorate. Damaged or weak nails can also be wrapped with fabric for reinforcement. Short nails can be lengthened using applied tips that are held in place by an adhesive, or, by using materials that are applied to the natural nail and build onto the end, using molds or forms to aid the shaping of the extension [3,4,5,6]. The function and service life of the enhancements vary with the chemistry of each.

The internet provides information on all the product types. Application techniques, both written and video are available in English and other languages [7,8]. Safety data sheets, lists of ingredients, basic chemistry explanations, advantages and disadvantages,

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[1] The basic methacrylate monomer products that MPA represents are Methacrylic Acid, Methyl Methacrylate, n-Butyl Methacrylate, iso-Butyl Methacrylate, Ethyl Methacrylate, and 2-Ethylhexyl Methacrylate. For additional information, visit mpausa.org.

[2] MPA's policy position can be found by clicking this link.

including health hazards and protective measures, are also readily available online and in publications targeting salon technicians and fashion-conscious consumers. There is no shortage of information in multilingual print or video media. This paper references only a fraction of what is available. To aid the reader, links are provided in the list of sources whenever possible.

Although the author understands that MPA members do not manufacture nail products, MPA is generally aware of the use of methacrylate monomers and polymers in the cosmetic industry. This review was requested by MPA to better understand this industry, and is intended to outline how methacrylate monomers, and methacrylate polymers and copolymers are, or are not, associated with commonly used nail enhancement types. It outlines the basic chemistry, availability, and application procedures, utilizing the readily accessible sources of information currently available to nail salon professionals and the general public. It does not aim to be fully comprehensive of all available materials but rather, aims to synthesize key information available online. It only summarizes the best information currently available to the author regarding methacrylates in nail products. Neither is this review intended to be a guide to application of nail products. Information on application processes is only provided to help the reader understand the complexity of the systems and why they are often confused with one another. To aid the reader, particularly noteworthy information will be highlighted.

The Chemistry of Nail Enhancement Products, Similarities and Differences

Why nail enhancements? The consumer wants to achieve pretty, healthy nails, ideally using a product or process that does not take too long and is affordable. Chemistry provides some of the ways to achieve this.

With the exception of traditional nail polish, all of the nail enhancement products or systems are based on "acrylic" chemistry[3], using monomers, oligomers, and polymers derived from acrylic acid, methacrylic acid, or cyanoacrylic acid [5]. Generally, the term "acrylic nails" applies to nails formed by a liquid monomer and powder system that is mixed and immediately applied to the nail. "Gel" nails are also based on acrylic/methacrylic chemistry, but the ingredients are premixed so there is no separate liquid monomer component. Nail wraps and no light gels are based on cyanoacrylate polymerization. In this review, efforts are made to specifically identify particular chemicals where possible, as these chemicals and broader chemical groups (acrylates, methacrylates, and cyanoacrylates) have different uses and different chemical profiles.

The basic process used for the various acrylic nail enhancements is rapid (within minutes) formation of a polymer coating or polymer extension on a fingernail (or toenail). It is important to understand that there are two very different types of polymer in nail enhancements. One is the polymer formed during the application process. The other is a polymer powder which is inert, but, is necessary to provide structural support by being incorporated into the final coating or extension being formed [9]

[3] The original meaning of acrylic was "containing acryl," from acrolein, the sharp, bitter liquid in onions, rooted in the Latin words acer, "sharp," and olere, "to smell." It has broadened over time to include substances made by a chemical process, used for making many different things, for example fibers for cloth, resins, adhesives, fillers and paint etc. As such it includes a wide range of chemistry including acrylates, methacrylates, cyanoacrylates and polymers thereof with different physical, chemical and hazard properties.

Artificial Nails: “Acrylics” and “Gels”

The differences between “acrylic” nails and “gel” nails applications are, (a) the starting materials to form the enhancement polymer and (b) the initiation of the polymerization process [10,11]. It must be noted that in the marketplace the term “acrylic nails” is not used in the chemical sense described above. It generically refers to artificial nails applied using the traditional two part liquid monomer and powder system that predated the development of gel nail systems.

Acrylic nails use liquid monomers as starting materials which join together to form the very long chains of polymer. Gel nails start the process with larger molecules, called oligomers, which are short chains of monomers. In gel formulations, these oligomers join together to form longer polymers.

Both acrylic and gel nail polymers are formed by free radical polymerization; however, acrylic nails begin to polymerize when the monomer liquid is mixed with the powder containing an activator chemical and source of free radicals. Gels contain all the necessary components, and use light energy to activate the source of free radicals and cause the polymerization of the oligomers to begin. See the Additional Resources list at the end of this document for links to a diagram of the free radical polymerization of PMMA and a detailed technical explanation of free radical polymerization.

The powders used in both the acrylic system and the gel systems are carriers to hold other ingredients needed to make the polymerization reaction proceed properly and provide strength to the enhancement. These powders are mostly small beads of inert acrylate or methacrylate based polymers or copolymers. These powders are formed using a specialized manufacturing process known as suspension polymerization. It produces grains of polymer with tightly controlled molecular weight and size. There are very small amounts of residual monomer trapped inside the beads. The polymers used in most powder for fingernail applications have molecular weights > 250,000 daltons. This is equivalent to chains of more than 2500 MMA molecules. The beads formed are in the range of 50 – 80 microns [5,12,13]. For comparison, a human hair is about 100 microns in diameter. Two types of suspension polymerization are emulsion and solution polymerization. Emulsion polymerized polymers contain 0.01–0.05% residual monomer, while solution polymerized PMMA contains 0.1 – 0.9% residual MMA, with estimated typical residuals of 0.3% [14].

Consumer Concerns

There is understandable concern related to health effects associated with the chemicals and use of light lamps in nail enhancement products, as well as damage to nails and finger tips that can be caused by both the application and the removal of these enhancements [12,14,15]. Harsh abrasion of the nails during preparation for product application or during removal of the hardened enhancements can weaken or damage the nail plate (area of nail adhered to finger). Solvents can cause dehydration of the nail and surrounding tissue. Skin sensitization (contact allergy), skin irritation, and respiratory irritation can be caused by methacrylates and other components of the systems [12,16,17,18,19,20]. Manufacturers provide product instructions and users are urged to follow directions carefully with regard to preventing skin contact and having adequate ventilation during use.

Methacrylate Esters

Methacrylate esters are formed by reacting methacrylic acid with an alcohol; for example, the alcohol used to form MMA Is methanol. Methacrylate esters are important in this discussion because early modern nail enhancement products depended largely on methyl methacrylate (MMA) monomer as their main ingredient. These products were often referred to as "porcelain nails" because they used the same material as dental fillings [21,22]. By the mid-1970s, the US Food and Drug Administration (FDA) received a number of complaints (including severe irritation, fingertip numbness, and allergic dermatitis) related to the use of MMA in artificial fingernail applications that it took action against several manufacturers of these products. Although there is no specific law preventing the use of MMA, FDA can take legal action against products that contain materials, like MMA, that it considers hazardous and inappropriate for a particular use [23,24,25]. Since then, ethyl methacrylate (EMA) or other methacrylate monomers have replaced MMA as the monomer in what are now commonly called “acrylic nails” [5,26].

MMA was once the preferred liquid monomer used in acrylic nails, but most salons and product manufacturers now use EMA and other related monomers. They do not use MMA. Various organizations and companies advise consumers to read labels carefully and ask about the ingredients used in the salons they frequent.

MPA strongly recommends, as reflected in its position paper, that consumers do not use nail products that contain intentionally-added methacrylate monomers. MPA is aware that a Cosmetic Ingredient Review Panel (CIR) considers methacrylate monomers other than MMA safe for use when applied by trained technicians and all contact with the skin is avoided. CIR recognizes that these chemicals can cause contact dermatitis and skin sensitization. Their conclusion included the stipulation that “Products containing these ingredients should be accompanied with directions to avoid skin contact, because of the sensitizing potential of Methacrylates.” [13,27]. MPA disagrees with the CIR position. MPA does not support the use of MMA or other unreacted methacrylate monomers in nail products because they are skin sensitizers and should not be used in contact with the skin or natural nails. The risk of contact between the unreacted liquid monomer and the skin cannot be avoided entirely [28].

Textbooks and consumer information bulletins provide warnings against the use of MMA and give some suggestions on recognizing if MMA is being used [5,24]. Many websites and blogs reinforce these messages. As an example, the Gel-Us Nail Studio website [29] is one of many that stresses avoidance of MMA containing brands and also includes the following admonition:

> ”Report the Use of MMA - If you know of someone who is using MMA containing products, or suspect that someone is using them in a salon, report your findings to your local State Board of Cosmetology and the U.S. Food & Drug Administration. You may also file a report with the Nail Manufacturers Council at (3l2) 245-1595”

Methacrylate Polymers

Polymethyl methacrylate (PMMA) is not the same as MMA [30]. Polymers are very long chains of molecules. Polymer properties depend on the way they are formed. MMA molecules can be initiated to react with other monomer molecules to form acrylic polymers for many different applications. PMMA in its final form can be sheets or cast forms or beads/powders [5,31]. If MMA is the only monomer used, the resulting homopolymer is PMMA. The same applies to EMA to form polyethyl methacrylate (PEMA). If more than one monomer is incorporated into the chain, then these are called copolymers and named accordingly. When monomers react and chains are formed by simply adding on to the end of a chain, like railcars in a train, then long snakelike polymers are formed which have poor solvent and impact resistance [5,12].) Monomers with more than one reactive site can be added to the reaction, allowing the monomers join together in a 3-D netlike structure, a stronger structure than the row of head-to-tail connections they would otherwise create [9,12]. The differences in molecular weight and physical and chemical properties also make the health effects of polymers different from their monomers.

PMMA powder is among those used in a variety of medical devices approved for use by the US Food and Drug Administration (FDA). It has been used in bone cement and filler, as well as intraocular lenses for over 50 years. More recently, PMMA was approved for use in dermal fillers[4]. PMMA beads are tiny, round, smooth particles that are not absorbed by the body [32,33,34,35]. The data FDA used to support the use of PMMA polymer in medical devices like bone cement was also used to support the safety of the powder in nail and other cosmetic applications [13]. The FDA website includes the following information that explains the differences in the reactions to monomers and polymers and helps explain why the efficiency of the polymerization process is very important in nail products and why artificial nails which rely on a polymerization reaction on the nail itself can be hazardous [30,34].

> "Artificial nails are composed primarily of acrylic polymers and are made by reacting together acrylic monomers, such as ethyl methacrylate monomer, with acrylic polymers, such as polymethyl methacrylate. When the reaction is completed, traces of the monomer are likely to remain in the polymer. For example, traces of methacrylate monomers remain after artificial nails are formed. The polymers themselves are typically quite safe, but traces of the reactive monomers could result in an adverse reaction, such as redness, swelling, and pain in the nail bed, among people who have become sensitive (allergic) to methacrylates." [34]

There are two sources of residual monomer in nail enhancement systems.

The first, less well controlled, source of residual monomer is the incomplete reaction of the monomer liquid during the formation of the nail coating/extension. Because the reaction is incomplete and occurring as the polymer forms and hardens on the nail, this is a source of residual monomer with the potential to contact the nail and the skin. If skin contact is strictly avoided as instructed, the risk that concentrations achieved from this

[4] gel-like substances that are injected beneath the skin to restore lost volume, smooth lines and soften creases, or enhance facial contour.

source could induce contact allergy may be low, as noted above. However, since individuals with existing contact allergy have a heightened sensitivity exposure during application may be sufficient to elicit irritation or allergic responses in people who are already sensitized to methacrylates.

The second source is residual monomer in the polymers used in the PMMA or other powders. The trace amounts of monomer in these polymers must migrate to the surface of the bead before they can be absorbed. This migration happens very slowly. In nail applications, the monomer would then need to migrate from the surface of the encapsulated beads to the surface of the polymer coating/extension, Polymer powders generally have very low residual amounts of monomer, and would be an insignificant addition to the overall free monomer concentration. The risk that concentrations achieved from this source could induce contact allergy or elicit an allergic response is therefore considered very low [14].

Acrylic powders used in acrylic and gel nail formulations contain high molecular weight polymer beads that may contain trace levels of residual monomers at concentrations not considered hazardous to health

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Types and Components of Nail Products

Nail coatings, or nail enhancements, fall into two categories: those that harden upon evaporation of a solvent, and those that polymerize upon application [15,36]. This section is a summary of the currently popular types of nail enhancements. More information for each type, including additional components and application techniques, is provided in expanded sections to follow.

Traditional nail polish, top coats and base coats are evaporation-dried coatings. They do not use monomers to form a polymer coating during application; rather, the polymer is dissolved in the solvents. Thus, these are essentially solvent-based paints. They are widely available in the consumer market and in salons [4].

Liquid-and-powder “acrylic” artificial nail systems are based on methacrylates; now most commonly, ethyl methacrylate (EMA), isobutyl methacrylate (iBMA), or hydroxyethyl methacrylate (HEMA). While the liquid monomer for acrylic nails is primarily a low molecular weight (MW) methacrylate ester, it also contains other components, including inhibitors, cross-linking agents, hardness enhancers, UV absorbers, etc. When mixed with the powder component, the methacrylate monomer liquid undergoes free radical initiated polymerization to form a cross-linked matrix encapsulating the powder and pigments in the system. Typically, benzoyl peroxide provides the free radicals to initiate the reaction. The final cross-linked polymer is very durable [5,9,12,37,38].

The “acrylic nail” is the only enhancement type using a liquid methacrylic monomer component which is blended with a polymer powder by the technician before it is applied to the nail. As noted above, MPA asserts that unreacted methacrylate monomers are skin sensitizers and should not be used in contact with the skin or natural nails.

Light-cured gel products use acrylates and methacrylates. Mono- or polyfunctional monomers and urethane acrylate and/or methacrylate oligomers undergo cross linking polymerization when a photoinitiator like benzoyl isopropanol is activated by exposure to UV or LED light, forming a solvent resistant coating that can act like a polish or an artificial nail [10,39].

Gel nail products may contain methacrylate monomers; however, concentrations are much lower than liquid monomer products. Common ingredients are hydroxyethyl methacrylate and hydroxypropyl methacrylate.

Polygels combine oligomers from gels, polymers from acrylics, and polymers from lacquers. An acrylic powder polymer is suspended in gel and the finish is light cured after application to form a solvent resistant coating that can act like a polish or an artificial nail [39,40].

Shellac nails are a patented form of polish available at verified salons. Shellac polishes mix two types of nail coating: gel (for durability and nail protection) and traditional nail polish (for color and shine). This coating can be removed using solvent. The Safety Data Sheet (SDS) does not mention any methacrylate monomers; however, much of the formulation is listed as proprietary. The manufacturer website explains the system [41,42,43,44].

Wraps, no-light gels, dipped nails, and instant nail adhesives are based on cyanoacrylates, not methacrylates. The cyanoacrylate monomer is activated to polymerize when it comes into contact with moisture or a weak base, forming a polymer with characteristics appropriate for the intended function. These are not cross-linked polymers. The cyanoacrylate polymer penetrates the fabric in wraps, and encapsulates the powder in dipped nails. No-light gels contain thicker viscosity cyanoacrylate monomers that can be applied as a thin coat, like nail polish, over the entire nail plate or nail tips to reinforce or add strength. The cyanoacrylate based enhancements are not light cured. Kits for the various applications are available in the consumer market and in salons [5; 6,45,46,47].

Of the nail enhancements listed above, only the traditional nail polishes do not involve any polymerization reactions.

The Issue of Odor

The odor of the materials used in nail enhancements can add or detract from the overall manicure experience. The odors associated with the products emanate from the low molecular weight volatile components, monomers and solvents and added fragrances [5].

The sharp odor associated with traditional acrylic nails is generally the monomer liquid. Gel products have the advantage of low odor because they are based on less volatile components. They also do not begin to polymerize as quickly as the mixed acrylic, allowing more sculpting time for the technician. In addition to oligomers and copolymers, some gel nail products contain lower molecular weight methacrylate monomers, but in smaller quantities than in the liquid monomer used for acrylic nails. The finished nail is usually not associated with any odor. Measurements of EMA residual from a properly light cured laboratory cosmetic nail gel formulation were 0.1 % or less [48].

Not all volatile materials can be detected by odor; some have no detectable odor, while others have very strong odors that are noticeable at very low concentrations in the air [5]. For example, people can detect the odor of MMA in the air at about 0.5 – 1.5 ppm [49]. This odor level is significantly lower than the typical occupational exposure limits (OELs) of 50 – 100 ppm set by regulators or industrial hygiene experts for this material [50]; therefore, smell and health hazard are not always related. The reliable way to assess what is in the air is to do air sampling or air monitoring [23]. Odor is not the only thing that affects air quality. Lack of adequate ventilation is of significant concern because of the presence of the mixtures of low levels of potentially hazardous chemicals in salon products and the common self-report of symptoms among nail technicians. To assess the adequacy of ventilation in salons, carbon dioxide levels were measured in 22 salons in the Boston area, indicating that 16 did not have adequate ventilation [51].

Air quality is important. The risk of health effects from inhaling any chemical depends on how much is in the air, how long and how often a person breathes it in. Common symptoms reported after short term indoor exposure to household volatile organic compounds include eye, nose & throat irritation, headaches, nausea/vomiting, dizziness, and worsening of asthma symptoms. People with respiratory problems such as asthma and people with heightened sensitivity to chemicals may be more susceptible to irritation from cold air and common irritants in the air such as smoke or chemical vapor/dust/fume and strong odors, such as perfume [52,53].

Published results of workplace air monitoring in nail salons included sampling for MMA. The studies were conducted between 2008 and 2012 with 22 salons in California and 12 in Utah participating. In all the salons but one, the air level of MMA was well below the OEL. Measured values ranged from less than detectable to 10.3 ppm in 53 samples, with 36 being less than 1 ppm. Only 2 samples, both from the same salon, exceeded the OSHA permissible exposure limit of 100 ppm [49,54,55,56]. Since this sampling was done, legislation banning MMA monomer in nail products was enacted in California (2015) and Utah (2017) [25,57].

Consumer Pressure for Less Hazardous Formulations

Manufacturers are under pressure to provide products with ingredients that are less hazardous and have a pleasant or no odor. To show their efforts in this regard, manufacturers tout what is not contained in their products through the use of so-called "FREE" lists. Notably, MMA and other methacrylates are not listed on any of the "FREE" lists. The lists focus on other ingredients under scrutiny by regulators for various health effects [58].

3-Free polish does not contain dibutyl phthalate, toluene or formaldehyde.

5-Free polish does not contain dibutyl phthalate, toluene, formaldehyde, formaldehyde resin or camphor.

7-Free polish does not contain dibutyl phthalate, toluene, formaldehyde, formaldehyde resin, camphor, parabens or xylene.

10-Free polish does not contain formaldehyde, toluene, DBP, camphor, formaldehyde resin, xylene and don't contain parabens, fragrances, phthalates, and animal ingredients.

Nail Enhancement Types – Additional Details

There is a wide range of professional and consumer nail enhancement products on the market and their method of application and the chemical composition varies considerably. Gaining an appreciation of this complexity is essential to better understanding worker and consumer exposure to chemicals during the application of these products.

Traditional Nail Polishes

"Regular" nail polishes, topcoats, and base coats contain no monomers and do not polymerize. They form coatings on the nail plate by evaporation of the solvent in the product [4,5,18,59].

There are 4 major types of ingredients in evaporation coatings: solvent, polymer, plasticizer, and colorants. Volatile or quickly evaporating organic solvents like butyl acetate or ethyl acetate or both make up most of the formulation. The polymers and plasticizers are dissolved in the solvent while the pigments are suspended in the formulation. The plasticizers improve flexibility and pigments provide the final color. Plasticizers that are commonly used are dibutyl phthalate and camphor. Two types of polymer are commonly used: nitrocellulose for hardness and shine, and toluene sulfonamide formaldehyde (TSF) resin for flexibility. These are not cross-linked polymers, so they dissolve easily. As the solvents evaporate, a smooth polymer film is left behind [4,15,18,60].

Nail polish will resist chipping and peeling if a good base coat is used. Base coats are more compatible with the nail plate and have more TSF resin to improve adhesion. Topcoats generally have high amounts of the nitrocellulose polymer with extra plasticizer and no pigments [61,62]. Clear topcoats thicken the applied coating, strengthening it and enhancing the gloss.

There are many different formulas for nail polish, providing variety in colors and finishes such as matte, glossy, or pearly. Some add ingredients for nourishing the nails or assisting with hardening. Nail hardener formulations can contain up to 3% formaldehyde, although more than 1% concentration can harm the nail by producing coatings that are too rigid. Formaldehyde-containing hardeners may cause an allergic response in some users, making them sensitive to the small amounts of residual formaldehyde in TSF resin [5,12,60]. Hypoallergenic polishes contain polyester or toluene sulfonamide epoxy resin in place of the TSF resin [5].

Traditional nail polishes have been widely used for decades. They are readily available in local drug stores, department stores, beauty salons, and via internet sales. These liquids are generally supplied in small bottles which also contain an applicator brush.

The general procedure is first to apply a base coat, then applying two color coats of polish and finally, applying a top coat. The polish is allowed to dry for a few minutes after each layer is applied. The mechanism here is simply to air dry. Once the solvents have evaporated, the polish is dry and cured. Because the polymers are not crosslinked in these products, polishes are prone to chipping and are readily dissolved by removers [18]. These coatings are temporary, generally lasting a few days to a week.

Methacrylate monomers are not found in traditional nail polish.

Acrylic Nails

Liquid and Powder Artificial Nail Building Products

The liquid is primarily monomer. Currently, ethyl methacrylate or isobutyl methacrylate is used in combination with other monomers, catalyst, UV absorbers and inhibitors. Inhibitors prevent the monomer from gelling and provide shelf life. UV absorbers prevent yellowing. The catalyst is the activator that causes the free radicals to form, and controls the speed of the reaction, once initiated. Catalyst balance is important to get a reaction that occurs at the right speed, not too fast or too slow [9]. Catalyst is approximately 1% of the monomer formulation [5].

The odor commonly associated with liquid monomer is due to ethyl methacrylate. The liquid phase also includes cross-linking monomers, poly-functional molecules such as ethylene glycol dimethacrylate, which are added to strengthen the polymer. In odorless acrylics, ethyl methacrylate is replaced by methoxyethoxy ethyl methacrylate, a larger, less volatile molecule [26,63]. While the methacrylate monomer is the primary component, other ingredients listed in commercially available liquid preparations include: N,N-Dimethyl-p-toluidine, 2-(2-hydroxy-5-methylphenyl) benzotriazole, triethylene glycol dimethacrylate, 2-hydroxy-4-(octyloxy) benzophenone, (2H-benzotriazol-2- yl)-4,6-ditertpentylphenol. The Safety Data Sheet (SDS) for the liquid phase will contain more information on the product components than the product label [64,65,66].

The powder phase consists of a polymer, often PMMA, whose particles act as an inert carrier for the other components, including an initiator which is required for the final product to form and cure. Optional ingredients include UV absorbers to prevent yellowing, colorants to tint or brighten the finished product, and titanium dioxide for white acrylic. The initiator in acrylics is benzoyl peroxide which, when heated, acts as source of free radicals and initiates the polymerization of the EMA monomer. This polymerization begins when the liquid and powder are mixed and exposed to air [9,30,67].

The long chain polymers encase the powder polymer beads which strengthens the final acrylic nail. Properly applied finished nail enhancements typically contain 33- 40% polymer powder. Instructions state that it is essential that the proper mix of liquid and powder be attained for a suitable finished nail. If the mixture is too wet, the artificial nail will not have enough powder, leading to cracking and lifting due to increased shrinkage. In addition, excess liquid can contribute to development of allergic reactions due to increased monomer contact with the nail and surrounding skin. If the mixture is too dry, the nail will not adhere properly because the ingredients in the liquid control adhesion [5,67].

The sculpting application process starts with cleaning the natural nail and priming the nail surface to promote adhesion.

Primers are available in two types, non-etching and etching. The non-etching type works like double-sided tape; one side of the primer is very good at sticking to the natural nail, and the other end is equally attracted to the acrylic polymers used in the artificial nail. Isopropyl-idenediphenyl bisoxyhydroxypropyl methacrylate, hydroxyethyl methacrylate, and carboxyethyl acrylate dissolved in ethyl acetate are example materials used in non-acid primers [68,68,70].

The etching types of primers are acids, such as methacrylic acid, which actually dissolve a thin layer of the nail itself. This etching process allows the acrylic to adhere to the nail better. The etching primers are more commonly used than non-etching. Of note, in 2001 the Consumer Product Safety Commission required that all products with more than 5% methacrylic acid be supplied in childproof containers [12].

After the nail is prepped, the resin is mixed, a form is placed over the nail to hold the resin in place and the mixture is applied to the nail. The resin is sculpted to look like a natural nail. When the resin hardens the form is removed. When the nail is dry, it is filed into shape. Polish can then be applied.

Nail professionals recommend that these nails be removed at a salon. The process involves filing the surface of the acrylic and soaking for several minutes in acetone and gently prying softened polymer off the nail, repeating the process as necessary until all is removed. Nails should then be buffed and oil applied. Attempting to pry or rip the nails off can cause serious damage to the natural nail [17].

Application guides and training materials caution technicians to strictly avoid getting any of the acrylic monomer materials on the skin or cuticle of the client or on their own hands. If contact does occur it should be immediately removed with a clean cotton swab or cloth [12,13,16].

Methyl methacrylate (MMA) was once commonly used as the monomer in acrylic nails but had recognized drawbacks. Years ago experience showed that it produced artificial nails that are too rigid, required damaging abrasion to the nail plate to adhere properly, and were extremely difficult to remove [5]. Training guides and methacrylate producers caution against the use of unreacted methyl methacrylate in nail products that come into contact with the nail plate or the skin [5,24,28]. Additionally, contact between the liquid monomer and the skin or nail bed can cause contact (skin) allergy. In response to consumer complaints and the number of cases of allergic contact dermatitis associated with the use of liquid MMA, FDA determined MMA to be unsuitable for this use. Since the late 1970s MMA is no longer used in this application by responsible manufacturers [34]. Now, many states also specifically prohibit the use of pure MMA in nail salon applications [57] (See Table 1.).

Table 1. Year legislation banned MMA in nail products by state

State	Year	State	Year
Alabama	2017	Montana	2015
Arizona	2017	New Hampshire	2018
Arkansas	2016	New Jersey	2012
California	2015	New Mexico	2018
Colorado	2018	New York	2018
District of Columbia	2017	North Carolina	2018
Delaware	2017	Ohio	2016
Florida	2018	Oklahoma	2012
Illinois	2014	Rhode Island	2018
Iowa	2016	South Dakota	2017
Kentucky	2018	Tennessee	2018
Louisiana	2018	Texas	2006
Maryland	2018	Utah	2017
Michigan	2018	Washington	2017
Mississippi	2017	Wisconsin	2012
Missouri	2013		

Liquid and powder acrylic nail systems are the only products with high concentrations of liquid methacrylate monomer. The PMMA powder does not react with the monomer; it is needed to add strength to the finished nail as well as acting as a carrier for other product components.

Gel Nail Products

Light-cured gel products are based on acrylate and methacrylate chemistry. Mono- or polyfunctional acrylate or methacrylate monomers and urethane acrylate and/or methacrylate oligomers undergo cross linking polymerization to form the final nail coating or extension. Gels are formulated to provide application specific characteristics. The length and density/tightness of the final polymer determines its hardness, porosity and permeability to solvents. The polymer forming ingredients are premixed with the polymer powder for optimum reaction efficiency.

Ingredients listed for commercially available hard gels include: Di-HEMA trimethylhexyl dicarbonate, trimethylopropane trimethacrylate, hydroxypropyl methacrylate, PEG-4 dimethacrylate, p-hydroxyanisole, hydroquinone, trimethylhexyl dicarbonate, triethyleneglycol trimethacrylate, bisphenol A-glycidyl methacrylate, triethyleneglycol divinyl ether, benzoyl isopropanol and pigments [71,72]. The example monomers and oligomers in this list are less volatile and provide more reactive sites than ethyl methacrylate, the monomer used in many acrylic liquid and powder systems. Some gel nail products also contain EMA in addition to oligomers and copolymers. Measurements of EMA residual from a properly light cured pharmaceutical nail gel formulation were 0.1 % or less. [48]

Gels can provide a more consistent final product than liquid and powder acrylic systems because the ingredients in the gel have been compounded by the manufacturer using the appropriate proportions of monomer, oligomer, initiator and the other additives that help the gel remain workable, adhere to the nail, harden properly and resist yellowing [10,73].

As with acrylic liquid and powder nails, the chemical reaction is free radical polymerization. In the case of gels, however, it begins when a photoinitiator, for example, benzoyl isopropanol or benzoyl peroxide, is activated by exposure to UV or LED light [65]. Traditional UV "hard" gels are formulated using lower MW oligomers which form tighter crosslinks, making them nonporous to provide the hardness and decreased permeability that provides the high solvent resistance [10,73]. Structure gels and soak off gels are compounded using higher molecular weight oligomers and monomers, generating longer, less dense polymer chains [10]. Additional photoinitiators are used in the soak-off gels so they can cure under LED lamps [74]. Gel coatings are set in just one or two minutes when exposed to UV light. Compared to "acrylics", they are strong, more flexible and odorless [75].

Increasing the porosity of the final polymer allows solvents to penetrate and soften the cured products for removal. This explains why gel polishes and some structural gel extensions are removed with acetone or specially blended solvent mixtures [5.] In contrast, hard gels are intended to be filed off, like acrylic nails. Peeling off a gel manicure can do serious damage to the surface of the nail. Nail experts advise to have hard gel nails removed at a reputable salon [73,76].

Structural Gels and Hard Gels

Two common nail enhancement gel types are structural gels and hard gels. These can be applied directly to the natural nail to provide additional strength. They are also used for sculpting directly onto the existing nail, or for attaching nail extensions.

Nail extensions can be formed using hard gel or structure gel. For sculpting, a form is placed under the natural nail to provide a base for the gel to be applied until the desired shape and length are achieved. Hard gel is generally used for building nails because it is more resistant to solvents and durable. Gels are also used to strengthen plastic nail tips or overlays that have been fixed to the nail with an adhesive [75].

Using gel, the finished extension is more flexible than an "acrylic" extension. In contrast to acrylic nails, which begin to polymerize and harden as soon as the monomer and powder are mixed and exposed to the air, gel does not harden until it is placed under the light source, allowing more time for the technician to shape the nail [77.] Even though gel nails are cured under a light or with an applied activator, the polymerization is not 100% complete. A tacky unreacted layer remains on the surface because oxygen acts as an inhibitor to the reaction. This sticky layer is removed using solvent [10,73]. Once the gel polymer is cured and cleaned, it can be filed into shape, buffed, polished, or decorated.

Gel Polishes

Gel nail polish is not the same as a structural or hard gel nail enhancement. Gel nail polish forms a softer, porous polymer that can be removed using polish remover. Some products called gel nail polish will air dry. Others need to be exposed to light or an activator to cure [46].

Light cured gel polish is a viscous liquid containing pre-mixed semi-solid monomers and oligomers and a photoinitiator. The photoinitiator absorbs light and transforms it into the energy required to initiate the polymerization process, forming the finished coating.

While under the light, the monomers and oligomers in the mixture combine to form long, interlocking (cross-linked) chains. The hardened gel is resistant to breakage, chipping, and smudging. Thin coats are applied and exposed to the light source after each application until the desired effect is obtained. Time under the light can vary from a few seconds to a minute depending on the brand. Thin coats allow the light to penetrate the gel and increase the efficiency of the polymerization. It also lessens the degree of shrinkage [5].

Unfortunately the term “no light gel” leads to some confusion because it is applied to two different types of product. Some products called no light gels are based on cyanoacrylate monomer formulations that harden when exposed to moisture and/or a catalyst or activator. Cyanoacrylates are also used in wrap resins and are discussed in the section on dipped nails [5,78].

Other products called no light gel polish polymerize using natural light, so they could be called natural light gels. The liquid applied is thinner than UV or LED light cured gels. They are solvent based, and are brushed on in thin coats. Each coat is allowed to air dry and then application is repeated. The application process is more time consuming as drying time, about 5 minutes, is required between coats. A product specific top coat containing a photoinitiator activated by natural light is applied and allowed to dry in the final step [39,46.79].

Some methacrylate monomers may be included in gels and gel-acrylic hybrids as cross linking agents or formulation modifiers. These are generally higher molecular weight, less volatile, and less concentrated than liquid monomer in acrylic nail preparations. PMMA or another inert copolymer powder is typically incorporated into the gel for strength.

Gel-Acrylic Hybrids

A gel-acrylic hybrid product uses oligomers from gel, polymers from acrylics and resins from traditional polish. It can be used as a natural nail coating or to sculpt and extend natural nails using common techniques like the use of forms. The gel provides an all in one format, so measuring and mixing are not required. As a gel, it remains pliable until cured, allowing time for the technician to achieve the desired shape. It comes in a tube and is applied as a bead, rather than a brush-on gel. These materials require curing under a lamp, either LED or UV. Finished nails are considered lightweight, flexible, and strong [3,40]. They are solvent resistant, and removal is best achieved by filing in a salon by a qualified technician [80].

Ingredients listed on product Safety Data Sheets include acrylates copolymer, trimethylbenzoyl diphenylphosphine oxide, polyurethane acrylate oligomer, hydroxyethyl methacrylate, polymethyl methacrylate, trimethylolpropane trimethacrylate esters, and dimethicone, confirming the blended technology. Gel-acrylic hybrids are considered to benefit from the lack of volatile materials and do not have the odor associated with acrylic nail preparation [81,82].

The product was developed to be easy to apply by a professional or a novice. A bead of product is applied to the nail and gently brushed and patted into shape. Another component of the system is a solution, often called a slip solution, applied to the brush to prevent the brush from adhering to the surface of the gel. This slip solution is a mixture of solvents, which could include isopropanol, acetone, and isobutyl acetate [40,83,84,85].

The instructions for application are straightforward. Place a bead of product in the middle of the clean dry nail. Using a brush dipped in slip solution, shape onto the nail and cure under the light. If extending the nail, add a bead of white to nail tip, brush into shape using a mold and cure. File to remove excess white and make it smooth. Apply topcoat or colored finish [80,83].

Dipped Nails

Dip systems are similar to, but not the same as, acrylic nails. They are not used for extending length on the nail. They are used to apply a color coating to natural nails and nails that are lengthened with applied tips. Dip systems require a series of liquid and powder applications but do not require a UV or LED light to cure [59,86,87].

The basic process requires at least 3 components: base liquid, acrylic powder(s), and final dryer coat. More complex kits also contain a base primer and additional topcoat. The liquid base is a cyanoacrylate formulation that polymerizes quickly when it comes into contact with moisture in the air or the nail [12]. It serves as an adhesive to hold the powder in place. It also can contain formulation specific additives [88]. The powders contain many of the same ingredients as those used in acrylic nails, i.e., PMMA, benzoyl peroxide, pigments and other additives formulated to work with the liquids in the specific kit [89]. The final liquid is generally described as a sealer/activator and contains solvents and a polymerization accelerator such as N,N-dimethyl-p-toluidine [59,90].

The general procedure involves applying a base liquid in a thin coat after which the nail is dipped into a container of the powder. The powder can be clear or pigmented. This step can be repeated a few to several times until the desired coating is achieved. Finally, the dryer/activator liquid is applied. A separate finishing step with a topcoat is also available in some kits. There is no UV or LED light curing required. See typical application instructions outlined below [11,87].

Chemicals are not the only reported cause for concern for nail health. There is conflicting information on the potential for the spread of bacteria/fungi/viruses if all clients dip into the same pot of powder at a salon. Use of individual dipping dishes is frequently recommended, with excess powder discarded, not returned to the original container. Alternative application methods suggested include brushing or sprinkling the powder on the nails [12,86,91]. No definitive data were found to support or refute the ability of pathogens to live in and be spread via the powder. Instances of nail fungal infections associated with dipped nails are reported. It is uncertain if the procedure caused the infection or exacerbated an existing condition [93,94].

The dip nail kits commercially available have at least 2 but often 4 or 5 different liquids which may not be interchangeable between suppliers, despite having similar names. For example, activator and top coats are specially formulated to work together and must be used as directed.

Typical application instructions include application of a nail prep for adhesion, followed by a base coat and powder dip. Base coat and colored powder applications are repeated until the desired effect is achieved. Finishing can include another clear coat, sealer/dryer, and top coat [87,92]. Removal of dipped nails is more difficult than for traditional nail polish. Like gel nails, the finished dipped nail coating can be removed by immersion in nail polish solvent for 15 – 30 minutes, sometimes longer. Nail experts recommend that removal be done by a professional in a salon. Attempting to scrape or peel off this coating can result in nail damage [11,86].

Dipped Nail and Nail Wraps are not based on methacrylate polymerization. The cyanoacrylate adhesive in these systems may contain some higher molecular weight alkyl methacrylate monomers as formulation modifiers. They do not contain lower molecular weight alkyl methacrylate esters such as MMA, EMA etc. PMMA or other copolymer powder beads are often a component of these systems.

Nail Wraps

Nail wraps have been in use for over 30 years. They are thin products originally made from fabrics e.g., paper, silk, linen, fiberglass, mesh, or more recently, from thin layers of decorative vinyl or cured polish, which are applied to the nail for extra reinforcement either as a natural nail coating, an embellishment, or as an extension. Fabrics applied are generally sealed with resin after application and shaping. These products are useful for individuals allergic to acrylic nails or primers or who have weak or damaged nails [6,36,95]. It has been reported that the nail wrap technique is time consuming and accounts for approximately 2% of the worldwide market [48]. It is unclear if this applies only to the salon technique rather than the consumer market “place and press” wraps. Of note, vinyl stickers are also available as place and press embellishments but are not functionally the same as nail wraps [96].

Available nail wrap kits vary from simple place, press, and trim appliances to multi component, multi-step systems. The multistep systems include components called resin or glue, resin activators or catalysts, and the wrap fabric or film. Some systems encase the fabric in gels that need to be cured under a light. (See the section on light cured gels for more information on the light cured products.) Polish can be applied after the wrap is shaped and set. Typical application procedures for the products are described below.

Traditional Nail Wraps

The liquid resin mixture of traditional nail wraps is based on cyanoacrylate monomers which can polymerize in the presence of moisture or with the use of an activator. Activators, sometimes called catalysts, are generally weak alkaline substances which may be listed as aromatic amines. They may be diluted in a solvent. Some catalyst free systems use the moisture present in the nail plate to initiate the curing and hardening of the coating polymer [5,36.95].

Instructions state that the resin must fully penetrate the fabric. The polymer encased fabric is intended to provide a stable, flexible coating. The cyanoacrylate polymers formed are not crosslinked. They form coatings that are susceptible to moisture and can be weakened by prolonged exposure to moisture. They can be removed by soaking for several minutes in an organic solvent, for example acetone [5,36,95].

According to instructions, the process of curing must be controlled to allow the polymer to form slowly and prevent excessive heat generation. The polymerization process is an exothermic reaction and rapid curing can cause enough heat to cause pain and damage the nail bed. In addition, under too fast or ‘shock” curing conditions the polymer coating contains many microscopic cracks, which weaken the wrap and provide an undesirable cloudy white finish rather than the expected clear, strong, and flexible coating [5].

Typical application procedures include prepping the nail to remove shine, application of a base coat of resin then accelerator and the chosen fabric on nail. Fabric is trimmed to fit and resin applied to saturate the fabric followed by a spray of activator. Additional layers of fabric / resin / activator are applied as needed to achieve the desired strength. Filing, buffing and a top coat or polish complete the process [95]. Instructions include the use of respiratory protection when using spray activators.

Self-adhesive wraps made of nail polish or vinyl also require a nail prep step. These wrap types are provided in sizes to fit the nails. The adhesive side is exposed and placed directly on the nail and smoothed into position. Excess is trimmed and filed away. To add more shine, or make them last longer, a top coat can be applied [96.97].

* * *

Concluding Remarks by MPA

MPA believes that methacrylate esters, including MMA, in unreacted monomeric liquid form are not appropriate for use in any artificial nail products. The corrosive properties of the acid and skin sensitization properties of the esters, reflected in past reports of injury due to their use in some nail products, indicate their use in such products should be restricted. The review above indicates that in many nail products, the lower molecular weight methacrylate ester monomers are no longer being used or are used in limited amounts. However, the review also shows that the use of nail products provides a source of exposure. For many years, MPA members have recommended that MAA and its esters in their unreacted monomeric liquid form should not be used in artificial nail products.

MPA is an association of U.S. manufacturers of MAA and its esters, whose members include Röhm America LLC, Arkema Inc., Lucite International, and The Dow Chemical Company. MPA and its members have product stewardship programs to support appropriate use of the chemicals they market

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Note: The websites referenced below were accessed during the month of March 2020 and the text reflects information available at that time.

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Additional resources:

Some websites that have SDS on nail products:

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