Methyl Methacrylate (MMA) in Cosmetic Nail Preparations
September 2009

Introduction

Liquid methacrylate monomers are used in the cosmetics industry in artificial nail preparations. The unreacted liquid methacrylate monomer is mixed with a methacrylate polymer powder at the time of application, and painted onto the nails. A cross-linking chemical reaction occurs between the monomer and the polymer mix, and the mixture hardens very quickly. The resultant nail can be filed, ground, and polished.

In the past, methyl methacrylate (MMA) monomer was used widely in acrylic nail preparations, however, due to concerns over adverse health effects of the chemical when used for this purpose, its use has now largely been replaced by other methacrylate esters, particularly ethyl methacrylate (EMA), which is considered to have lower toxicity than MMA. Concerns about MMA in cosmetic products relate only to MMA monomer (liquid MMA). MMA-based polymers do not have the same toxicity profile as MMA monomer.

Recently, concerns about possible use of MMA monomer in the Australian cosmetic nail industry have been raised in the media and in public enquiries to NICNAS. As a result, NICNAS has investigated the use and safety of MMA in the cosmetic nail industry and the adequacy of current regulatory controls in Australia. This information sheet presents the major findings of this review.

Chemical Identity

<table>
<thead>
<tr>
<th>Common name:</th>
<th>Methyl methacrylate (MMA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical name in AICS</td>
<td>2-Propenoic acid, 2-methyl-, methyl ester</td>
</tr>
<tr>
<td>IUPAC chemical name:</td>
<td>Methyl 2-methylacrylate</td>
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</tbody>
</table>
**Synonyms:**
- Methyl methacrylate monomer
- Methacrylic acid, methyl ester
- 2-methylacrylic acid methyl ester
- methyl 2-methyl-2-propenoate
- 2-methyl-2-propenoic acid methyl ester
- 2-(methoxycarbonyl)-1-propene
- methyl alpha-methacrylate
- methylpropylene-2-carboxylate
- acrylic acid, 2-methyl-, methyl ester

**Structural formula:**

```
\[
\begin{array}{c}
\text{H}_2\text{C}\\
\text{H}_3\text{C}\\
\text{O}\\
\text{O}\\
\text{CH}_3
\end{array}
\]
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**Molecular formula:** $\text{C}_5\text{H}_8\text{O}_2$

**Molecular weight:** 100.12 g/mol

**CAS registry number:** 80-62-6

MMA is a colourless, volatile liquid, with a characteristic odour that has been described as fragrant, fruity, acrid and pungent, or onion-like.

The cosmetic ingredients known as poly(methyl methacrylate) or methyl methacrylate crosspolymer are solid polymeric substances derived from methyl methacrylate monomer, and do not share the toxicity concerns for methyl methacrylate monomer.
Import, Manufacture and Use of MMA in Australia

MMA is listed on the NICNAS High Volume Industrial Chemicals List (HVICL). It is imported in volumes of greater than 20 tonnes per annum. No manufacture in Australia has been reported. The primary use is as a monomer in formation of materials such as plastics and paint polymers. MMA monomer is also a component of two-part adhesive glues and cements (up to 60% MMA), in sealant formulations, in floor coatings (~20% MMA), in dental prostheses and fillings (80-90+% MMA), and in surgical implants (e.g. orthopaedic bone cements).

A NICNAS call for information on the cosmetic uses of MMA and EMA confirmed that EMA is far more prevalent in the cosmetic nail market than MMA. Only two respondents indicated that they import MMA for fingernail enhancement purposes - one at 5 kg per annum in nail polish at 20% concentration, and the other as part of an acrylic gel. No Australian distributors of MMA for cosmetic use have been identified. However the possibility of importation by non-respondents to the NICNAS call for information, including importation from internet sources by small operators, or diversion from amounts imported primarily for dental or industrial use, cannot be ruled out.

There is anecdotal evidence that MMA has been found in the fingernail industry in Australia, particularly in cheaper imported products in both beauty salons and nail kits for home use. It has been reported that such products are often inappropriately labelled or unlabelled, and that staff using them have been unaware of both the product’s content and of any safety requirements. The Australian Professional Fingernail Industry Association (APFA) has reported the availability of home fingernail enhancement kits containing liquid acrylic monomer, and the presence of MMA in these products cannot be ruled out. A search of the internet found artificial nail products containing “acrylic glue” and “acrylic liquid” for sale at Australian on-line pharmacies.

Potential Exposure to MMA

Acrylic nail preparations are used in beauty and nail salons, and can also be marketed as kits for home use. The acrylic mixture can be ‘sculpted’ over a form attached to the natural nail plate at the end of the fingers to produce artificial nails. It may also be applied over the top of pre-formed artificial nails that have been glued onto the nail plate, or onto the natural nail after preformed nail tips have been glued to the ends of the natural nail plate. A typical procedure may involve the following steps:

1. Initial preparation which could involve grinding off an old artificial nail
2. Application of antiseptic to the nail
3. Light buffing of the nail
4. Application of a dehydrant to the nail plate
5. Application of a nail primer to the nail plate (the primer not touching the skin)
6. Dipping a brush into a methacrylate monomer and then into a polymer powder to form a small ball
7. Placing the ball onto the nail
8. Patting the material towards the cuticle and nail edges without touching the skin
9. Shaping and contouring the nail
The application scenarios indicate that the most probable exposures relate to inhalation of vapour and short-term small volume skin contact in the immediate vicinity of the fingernail. Use of MMA in properly equipped nail salons will generally be under local exhaust ventilation, and the worker applying the acrylic monomer will be trained to avoid contact with the skin during application. However, as MMA is usually cheaper than other methacrylate monomers, it is more likely to be used in cut-price salons, which may be expected to be less scrupulous than more upmarket salons in training and use of safety equipment. It is also considered likely that consumers would have difficulty avoiding skin contact while using home “nail kits” single handed, particularly with the less preferred hand. Also, the presence of local exhaust ventilation in home applications is unlikely.

The consumer and the beautician would both be exposed to MMA vapour throughout the (often lengthy) procedure, making adequate ventilation a concern. For example, in beauty salons in the USA, mean concentrations of MMA have ranged from 5.2 to 21 ppm during the application of artificial fingernails. The level of MMA exposure is also affected by the quality of ventilation. In a study of downdraft tables used by American beauticians for the application of cosmetic artificial fingernails, there was a 14.5-fold difference between breathing zone methacrylate exposures while using different table designs (Spencer et al., 1997).

Health Hazard Information

There is a large amount of information available on the toxicity and health effects of MMA. The major sources of the following summary are reports by the European Chemicals Bureau (EU, 2002) and the International Program on Chemical Safety (WHO, 1998). A full independent hazard assessment of MMA has not been conducted by NICNAS.

Acute Toxicity

MMA is not considered to be acutely toxic by the oral route with LD50 (Lethal Dose, 50%) values in a variety of species of at least 4700 mg/kg bw (dogs). In rats, reported values are in the range of 7552-9440 mg/kg bw. The dermal LD50 for MMA in rats was > 5000 mg/kg bw. The 4-hour inhalation LC50 (Lethal Concentration, 50%) values ranged between 3750 and 7268 ppm in rats and mice. It has been postulated that this low acute toxicity is due to its rapid metabolism.

Irritation

Skin - MMA is severely irritating to rabbit skin, with desiccation, blanching and eschar formation seen in addition to erythema and oedema. In humans, 5% MMA produced skin reactions (erythema and eczematous dermatitis) in 18/20 volunteers.

Eyes - MMA application resulted in only mild conjunctival irritation in rabbit eyes, with signs persisting till day 2.

Inhalation - Respiratory irritation has been observed in both test animals and in humans following exposure to vapours of MMA. The concentrations resulting in irritant responses were not dependent on exposure duration. Animal studies showed respiratory irritation such as interalveolar congestion/haemorrhage, pulmonary vasodilatation and oedema at 100 ppm MMA (2-4 h), and specific nasal lesions following exposure to 400 ppm MMA. Recovery in rats exposed to MMA by inhalation was very slow; for example exposure for 4 weeks to 110 ppm MMA resulted in lesions that required 4 weeks to full recovery. Human data for occupational exposure indicated that respiratory irritation by MMA occurred at concentrations lower than 112 ppm.
Sensitisation

Skin - MMA has a moderate sensitising potential in experimental animals, with clear animal evidence of skin sensitisation by exposure to MMA. There are numerous human clinical reports of skin sensitisation response by MMA. There is also clear animal and human evidence of cross-sensitisation reactions between different methacrylate esters.

Inhalation - No evidence is available to indicate respiratory sensitisation potential of MMA.

Repeated Dose Toxicity

In a 2-year oral study in rats via drinking water, a No-Observed-Adverse-Effect-Level (NOAEL) of 146 mg/kg bw/day was established for increased relative kidney weights and decrease in fluid consumption in females only. In inhalation studies, respiratory tract effects were seen from 100 ppm, while systemic effects such as change in body weights were seen from 500 ppm, and effects were seen in the liver, kidneys, spleen, bone marrow and central nervous system at higher doses again.

Neurotoxicity

In an acute inhalation study using MMA, changes in neuronal activity in rat brains were seen at 400 ppm, while changes in behaviour and brain and nervous system chemistry were seen at 500 mg/kg bw/day in a 28-day oral repeat dose study. Malacia and gliosis of the brain were seen following exposure of rats to 1000 ppm MMA for 14 weeks. Human clinical reports indicate finger numbness and other neurological problems can be related to MMA exposure. It is not possible to correlate the degree of MMA exposure with the severity of neurotoxicity from these case reports.

Reproductive and Developmental Toxicity

Insufficient evidence is available to indicate whether MMA shows developmental or reproductive toxicity.

Mutagenicity and Carcinogenicity

MMA is not mutagenic in bacterial tests, but there is evidence of chromosomal damage at high doses in cultured mammalian cells. There are no carcinogenicity studies in animals and limited epidemiological evidence does not indicate a carcinogenic potential for MMA.

Cytotoxicity

The cytotoxicity of MMA has been demonstrated in many cultured cell lines, including several fibroblasts, periodontal ligament cells and human primary neocortical neurons. The cytotoxicity of MMA may be a contributing factor to its other toxic properties.
Other Health Effects

In addition to the direct toxicological concerns arising from use of MMA, other effects arise from the hard nature of the bonding layer when MMA is used. These include difficulty in removal, requiring mechanical grinding or drilling to remove old nails, or alternately 2-hour soaking in acetone. Mechanical damage can occur to the nail plate when impact occurs on the finished nail in use, due to lack of “give”. Painful breaking of the nail plate can occur. Infections around the nail plate may result from such damage. Anecdotal reports of nail deformity may be related to these effects of MMA.

Summary of Key Health Issues

The toxicity profile indicates that MMA is a severe skin irritant, has skin sensitising potential, is a respiratory irritant, and a mild eye irritant. There is no minimum sensitisation concentration – even low exposures to MMA may lead to sensitisation. Short-term small-volume dermal exposure to MMA on a repeated basis is likely to result in skin sensitisation rather than skin irritation. Symptoms of skin irritation and sensitisation may include swelling, redness, itching, burning, numbness, cracking of the skin, pain, skin rashes (including allergic contact dermatitis).

The saturated vapour pressures of MMA is much higher than the concentrations at which respiratory irritation have been observed, and accordingly there is significant risk of respiratory irritation during use without efficient ventilation systems. Symptoms may include teary eyes, sore throat, coughing, and irritation of nose or throat.

The particular hardness of artificial nails produced using MMA present a risk of physical injury from drilling and grinding of the nails, and breakage of the nail plate, and this is a strong cause for concern.

Current Regulatory Status

In the Workplace -

Hazard Classification

For occupational use in Australia, MMA is currently classified as a Hazardous Substance according to the Approved Criteria for Classifying Hazardous Substances [NOHSC:1008(2004)]. It is classified as hazardous at and above concentrations of 1%. It is listed with the following risk phrases in the Hazardous Substances Information System (HSIS):

- F; R11 Highly flammable
- Xi; R37/38 Irritant; Irritating to respiratory system and skin
- R43 May cause sensitisation by skin contact

MMA used in the workplace should be labelled in accordance with the National Code of Practice for the Labelling of Workplace Substances [NOHSC:2011(2003)]. It should be labelled with the above risk phrases as well as the following safety phrases:
Avoid contact with skin
Wear suitable gloves
If swallowed, seek medical advice immediately and show this container or label.

Exposure Standard

The following atmospheric contaminant exposure standards apply to MMA for occupational environments in Australia (note: 1 ppm = 4.16 mg/m³):

<table>
<thead>
<tr>
<th>Standard Type</th>
<th>Concentration</th>
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<tbody>
<tr>
<td>Time weighted average (8 hour TWA)</td>
<td>50 ppm (208 mg/m³)</td>
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<tr>
<td>Short-term exposure limit (15 min STEL)</td>
<td>100 ppm (416 mg/m³)</td>
</tr>
</tbody>
</table>

MMA’s odour detection threshold is 0.05 ppm and its odour recognition threshold is 0.34 ppm. Therefore, workers handling MMA will have sufficient warning to potentially toxic levels of MMA vapour, as its detection level is well below the TWA level.

Public Health

MMA for use in cosmetic preparations is listed in Appendix C of the Standard for the Uniform Scheduling of Drugs and Poisons (SUSDP) No. 21, Amendment 3 effective 1 May 2007 (NDPSC, 2007). The SUSDP classifies drugs and poisons and sets out legal requirements for the labelling of drugs and poisons that are sold to the public. Appendix C lists substances, other than those included in Schedule 9 (prohibited substances), considered to be of such danger to health as to warrant prohibition of sale, supply and use.

For non-cosmetic uses, MMA is listed in Schedule 6 (Poison – substances with a moderate potential for causing harm, the extent of which can be reduced through the use of distinctive packaging with strong warnings and safety directions on the label) except in preparations containing 1% or less of MMA as residual monomer in a polymer. Specific warning statements and safety directions must be included on the container label (NDPSC, 2007). SUSDP classifications are enforced through state/territory poisons legislation.

Cosmetics and toiletries manufactured in or imported into Australia must also be labeled in accordance with the Trade Practices (Consumer Product Information Standards) (Cosmetics) Regulations 1991, as amended. Under these Regulations, ingredients must be listed on the container or the product itself, if not packed in a container. Ingredients should be listed in descending order calculated by mass or volume. MMA must be listed by one of its English names.

International Regulatory Activities

USA

The Food and Drug Administration (FDA) took court action during the 1970s to remove from the market fingernail cosmetic products containing 100% MMA monomer, due to the risk of sensitisation and fingernail damage. No formal ban was enacted. In 2005, the FDA confirmed their belief that MMA monomer in cosmetic fingernail preparations is a “poisonous and deleterious substance”, and approximately 30 states of the USA
have banned or recommended against the use of MMA in nail preparations. (US FDA, 2005, 2006; MPA, 2002)

Canada
In May 2003, Health Canada issued an Advisory notice imposing a ban on the selling of all cosmetic nail products containing MMA, citing allergic reactions and irritation, and the possibility of painful tearing of the nail due to strong adhesive properties of MMA (Health Canada, 2003).

New Zealand
In July 2006, New Zealand’s Environment Risk Management Authority (ERMA) issued a Group Standard for Cosmetic Products that bans the use of MMA in cosmetics (ERMA New Zealand, 2006a&b).

Industry Activities

In the USA, the Cosmetic Ingredient Review has issued a statement supporting the FDA position. The Methacrylate Producers Association, Inc. has issued a position statement against the use of unreacted methacrylic monomers in liquid form in cosmetic products, citing skin sensitisation properties (MPA, 2002). The Nail Manufacturers Council of the American Beauty Association states that the use of MMA is unsafe and unwise, citing serious adverse skin reactions and permanent nail deformities, as well as painful breaking of the nail plate near the eponychium that may lead to infection (NMC, 2001).
Data Sources


