

The Science of Air Fresheners

Part 1: From the Product to the Air

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From the Product to the Air

- By design, certain ingredients in air fresheners must be highly volatile to achieve the desired “effect”.
- Some primary ingredients can react with indoor air to different degrees to produce other compounds.
- For adequate shelf life, most home care products, including air fresheners, require preservatives.
- To go from the product to the air, air fresheners typically require additional ingredients (e.g. oil).
- Once they reach the human body, multiple compounds can conspire together in the damage they cause or health risk they impose.



Primary
Ingredients



Secondary
Products



Preservatives



Carrier
Ingredients



Synergistic
Compounds

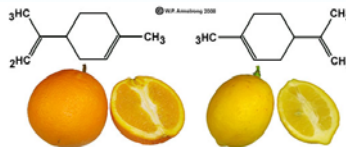
One or more of these classes of ingredients can pose unacceptable health risk even during “regular use”

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Primary Ingredients The Story of the Terpenes

- **The Terpenes**
 - Many ingredients used in air fresheners to produce fragrance are terpenes. Terpenes are unsaturated volatile organic compounds that occur in nature and are presumed to be safe.



- **But**
 - Many terpenes have been found to have serious health effects in reputable research studies.
 - Many terpenes are emitted from air fresheners at far greater concentrations than those found in nature.

Primary Ingredients The Story of the Terpenes

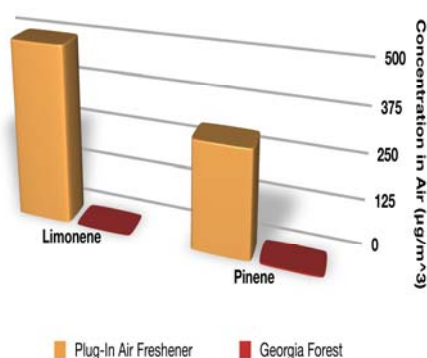
- **Serious Health Effects in Laboratory Studies**

- d-limonene is a weak animal carcinogen and α -pinene is a mutagen. ^a
- Both are respiratory irritants at higher concentrations. ^b

- **Emissions Far Greater Than “Natural”**

- Concentrations of d-limonene and α -pinene in Georgia Forest ^c are less than 1% of the concentrations found in a plug-in air freshener. ^{b,d}

Concentrations of Limonene and Pinene in Nature and in Plug-In Air Freshener



^a - Wallace, Lance et al. "Exposure to Volatile Organic Compounds" in *Exposure Analysis*, 2007 Boca Raton, CRC Press

^b - Beuc and ICRT "Emission of chemicals by air fresheners: Tests on 74 consumer products sold in Europe" 2005

^c - Hester, Ronald E et al. *Volatile Organic Compounds in the Atmosphere* 1995. Cambridge, The Royal Society of Chemistry

^d - Steinemann, Anne C. "Fragranced consumer products and undisclosed ingredients" *Environ Impact Assess Rev* (2008). (Pinene concentration is given as above 300 µg/m³)

Primary Ingredients The Story of the Terpenes

| Forest | Chemical | Concentration in Air (ppbv) ^a | Concentration in Air (µg/m ³) |
|--------------------|------------------|--|---|
| Georgia Forest | d-limonene | 0.08 | 0.44 |
| | α -pinene | 0.8 | 4.45 |
| Southwest Scotland | d-limonene | 0.016 | 0.09 |
| | α -pinene | 0.027 | 0.15 |
| | d-limonene | 0.04 | 0.22 |
| Rome Forest | α -pinene | 1.5 | 8.34 |

In contrast, typical concentrations of limonene and α -pinene in plug-in air fresheners are greater than 300 µg/m³. ^b

^a - Hester, Ronald E et al. *Volatile Organic Compounds in the Atmosphere* 1995. Cambridge, The Royal Society of Chemistry

^b - Steinemann, Anne C. "Fragranced consumer products and undisclosed ingredients" *Environ Impact Assess Rev* (2008)

Primary Ingredients The Story of the Aldehydes

- **The Aldehydes**

- Acetaldehyde and benzaldehyde are used as solvents in air fresheners. They capture all of the ingredients together for a homogenized release.

- **But**

- Both acetaldehyde and benzaldehyde are easily volatilized at room temperature and pressure.
- Acetaldehyde and benzaldehyde both have proven health risk to humans through inhalation. ^a



^a - Cassee, Flemming et al. "Changes in the Nasal Epithelium of Rats Exposed by Inhalation to Mixtures of Formaldehyde, Acetaldehyde, and Acrolein" *Fundamental and Applied Toxicology*, 29, 208-218 (1996)

Primary Ingredients The Story of the Aldehydes

- Volatility – concentrations of acetaldehyde and benzaldehyde have been found to be greater than 300 µg/m³ in plug-in air fresheners and in solid deodorizing disks for acetaldehyde. ^a
- Proven Health Risk
 - Benzaldehyde
 - Known -- respiratory irritant, carcinogen. ^b
 - Acknowledged -- classified as a toxin by the Federal Insecticide, Fungicide, and Rodenticide Act. ^a
 - Acetaldehyde
 - Known -- respiratory irritant, carcinogen. ^b
 - Acknowledged -- classified as a Hazardous Air Pollutant by the EPA therefore, exposure to it is not safe at any level. ^a
 - Both acetaldehyde and benzaldehyde attack respiratory receptors in the nose and can lead to a decrease in breathing frequency. ^b

^a - Steinemann, Anne C. "Fragranced consumer products and undisclosed ingredients" *Environ Impact Assess Rev* (2008)

^b - Cassee, Flemming et al. "Changes in the Nasal Epithelium of Rats Exposed by Inhalation to Mixtures of Formaldehyde, Acetaldehyde, and Acrolein" *Fundamental and Applied Toxicology*, 29, 208-218 (1996)

From the Product to the Air

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Secondary Products The Story of Formaldehyde

- **Formation of Formaldehyde**
 - Terpenes like α -pinene, d-limonene, linalool, and citronellol all react with transient compounds in the air. ^a
 - These reactions result in the formation of aldehydes, especially formaldehyde. ^a
- **Competitive Reaction Rates Indoors**
 - The hydroxyl radical is a by-product of the terpene/ozone reactions. Once formed, it has a faster reaction rate with various terpenes than ozone does. ^a
 - Ozone, reacts at rates competitive with species that contain unsaturated carbon-carbon bonds, while the hydroxyl radical, and NO_3 can react with most organic species found in air at rates that are competitive with air exchange rates in homes and buildings. ^{b,c}

^a – Destallants, Hugo et al. "Indoor Secondary Pollutants from Household Product Emissions in the Presence of Ozone: A Bench-Scale Chamber Study" *Environ. Sci. Technol.* 2006, 40, 4421 - 4428

^b – Micheli, Clifford S. et al. "Current State of the Science: Health Effects and Indoor Environmental Quality" *Environmental Health Perspectives* (2007) Volume 115

^c – Weschler, Charles "Chemical reactions among indoor pollutants: what we've learned in the new millennium" *Indoor Air* 2004, 14: 184-194

Secondary Products

The Story of Aldehydes

- **Aldehyde and SOAs**

- Formaldehyde, acetic acid, formic acid, acetaldehyde, propionaldehyde and glycolaldehyde are the products with the greatest concentration. ^{a,b}
- For a plug-in air freshener, formaldehyde yields ranging from 30 – 90% of the terpene concentrations were observed. ^c
- These reactions also yield high concentrations of secondary organic aerosols, which are known respiratory irritants. ^a

- **d-limonene and α -pinene Greatly Increase the Concentration of Products**

- Studies have shown that the d-limonene and α -pinene in air fresheners are the dominant species driving the formation of these products. ^b
- When d-limonene and α -pinene are not present, the concentrations of the aldehydes formed drop by 50%. ^b

^a– Destailants, Hugo et al. "Indoor Secondary Pollutants from Household Product Emissions in the Presence of Ozone: A Bench-Scale Chamber Study" *Environ. Sci. Technol.* **2006**, 40, 4421–4428
^b– Fan, Zhihua et al. "Ozone-Initiated Reactions with Mixtures of Volatile Organic Compounds under Simulated Indoor Conditions" *Environ. Sci. Technol.* **2003**, 37, 1811 – 1821
^c– Weschler, Charles "Chemical reactions among indoor pollutants: what we've learned in the new millennium" *Indoor Air* **2004**, 14, 184-194

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Ingredients

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Secondary
Products

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Preservatives

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Carrier
Ingredients

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Synergistic
Compounds

Preservatives Formaldehyde and Neolone

Formaldehyde and Neolone: are both used in air fresheners to prolong shelf life

| Freshener Type | Scent | Formaldehyde Emitted ($\mu\text{g}/\text{m}^3$) ^a |
|-------------------|----------|--|
| Liquid Diffusers | Orange | 6 |
| Aerosol Sprays | Orange | 1 |
| | Citrus | 3 |
| | Floral | 9 |
| Electric Diffuser | Cinnamon | 4 |

But...

- Formaldehyde is known to cause damage to the respiratory tract and it has a Toxicological Reference Value of $0.013 \mu\text{g}/\text{m}^3$.^a
- Neolone is a blend of a few chemicals, namely methylisothiazolinone (MIT) which is a potent neurotoxin.^b

a - Beuc and ICRT "Emission of chemicals by air fresheners: Tests on 74 consumer products sold in Europe" 2005
b - Du, Shen et al. "In Vitro Neurotoxicity of Methylisothiazolinone, a Commonly Used Industrial and Household Biocide, Proceeds via a Zinc and Extracellular Signal-Regulated Kinase Mitogen-Activated Protein Kinase-Dependent Pathway" *The Journal of Neuroscience*, 2002, 22(17): 7408-7416

Preservatives Formaldehyde and Neolone

• MIT (in Neolone)

- MIT primarily kills microorganisms growing in the product before they can contaminate the solution.^a
- MIT also has been shown to be toxic to cultured rat neurons *in vitro* and may have an effect on brain development in mice.^{a,b}

• Formaldehyde

- Formaldehyde is classified as a possible human carcinogen by the EPA, and a probable human carcinogen by ATSDR.^{c,d}
- The International Agency for Research on Cancer classifies formaldehyde as a known human carcinogen.^e
- It also has been shown that formaldehyde attacks olfactory receptors in the nasal cavity of mice.^f

a - Du, Shen et al. "In Vitro Neurotoxicity of Methylisothiazolinone, a Commonly Used Industrial and Household Biocide, Proceeds via a Zinc and Extracellular Signal-Regulated Kinase Mitogen-Activated Protein Kinase-Dependent Pathway" *The Journal of Neuroscience*, 2002, 22(17): 7408-7416
b - He, Kai et al. "Methylisothiazolinone, A Neurotoxic Biocide, Disrupts the Association of Src Family Tyrosine Kinases with Focal Adhesion Kinase in Developing Cortical Neurons" *JPET*, 2006, 317: 1320-1329
c - <http://www.epa.gov/ttn/atsw/hlthef/formalde.html>
d - <http://www.atsdr.cdc.gov/mhmi/mmg111.html>
e - http://monographs.iarc.fr/ENG/Health_cars/08-formaldehyde.pdf
f - Cassee, Flemming et al. "Changes in the Nasal Epithelium of Rats Exposed by Inhalation to Mixtures of Formaldehyde, Acetaldehyde, and Acrolein" *Fundamental and Applied Toxicology*, 29, 208-218 (1996)

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

Carrier Ingredients Benzene in “Plug-in” Products

- **Benzene**
 - Benzene is used in air fresheners to disperse the product into the air.
- **But...**
 - Benzene is a known carcinogen, and the EPA has stated that there is risk of getting cancer due to exposures of 1 $\mu\text{g}/\text{m}^3$ over one's lifetime. ^a
 - The IARC has linked exposure to benzene to the occurrence of many different types of leukemia in humans and ATSDR has also classified benzene as a known human carcinogen. ^{b,c}

| Liquid Diffuser Scent | Concentration of Benzene Emitted ($\mu\text{g}/\text{m}^3$) ^a |
|-----------------------|--|
| Peach | 4 |
| Orange | 7 |
| Spice | 8 |
| Vanilla | 8 |

^a - Beuc and ICRT "Emission of chemicals by air fresheners: Tests on 74 consumer products sold in Europe" 2005
^b - http://www.inchem.org/documents/iarc/iarc_supp7/benzene.htm
^c - <http://www.atsdr.cdc.gov/toxprofiles/tp3.pdf#qurise>

From the Product to the Air: Summary

- Limonene is a weak animal carcinogen, α -pinene is a mutagen, benzaldehyde and acetaldehyde are known carcinogens. All of these are respiratory irritants.  Primary Ingredients
- Formaldehyde and other aldehydes are produced due to reactions between the transient materials in the air and the terpenes presents in air fresheners. This can occur anywhere in the world due to the high ground level ozone concentrations world-wide.  Secondary Products
- Formaldehyde is a known carcinogen and a respiratory irritant. MIT, a chemical found in Neolone, has been proven to be a neurotoxin.  Preservatives
- Benzene exposure has been linked to multiple kinds of leukemia and is a known carcinogen.  Carrier Ingredients
- Once they reach the human body, multiple compounds can conspire together – will be addressed in next as: From the Air to the Body  Synergistic Compounds

The Science of Air Fresheners Part 2: From the Air to the Body

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