

FLORIDA CHEMICAL COMPANY, INC.



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August 18, 2004

Ms. Dorothy Shimer
Research Division
Air Resources Board
P.O. Box 2815
Sacramento, California 95812

Dear Ms. Shimer:

This letter is in response to the *Draft Report to the California Legislature, Indoor Air Pollution in California in response to Assembly Bill 1173* and the ARB welcoming of comments on this report. Florida Chemical understands the need to address indoor air quality and the removal of neurotoxins, carcinogens or reproductive toxins from building and consumer products used indoors. Our company is fully supportive of your effort, we have been providing industry leadership on this issue for over 60 years.

We have grave concerns about statements made in your draft report. Many of the statements made regarding d-limonene and citrus terpenes are simply false or misleading. Our company draws a clear distinction between scientific evidence and ill-conceived or mis-informed opinions about d-limonene and citrus terpenes. We have reviewed much of the reference data listed with this report. There is no data to substantiate the serious allegations made about d-limonene and/or terpenes in general. In fact, the authors of the research referenced in your report often come to completely different conclusions than your report implies.

Florida Chemical is proud of our position as the leading supplier of d-limonene and citrus-derived terpenes in North America. Citrus terpenes are naturally derived through the pressing of citrus peels in the juicing process. d-Limonene is a naturally occurring product from the citrus harvest. Our citrus terpenes are biogenic hydrocarbons found in house plants, oranges, and fruit juices to name a few sources; they are not synthesized from petroleum or coal. Our natural citrus by-products (such as d-limonene) have long been an alternative to many of the dangerous harmful chemicals identified in your report.

In fact, we were recently honored to be repeatedly listed in ARB's own suggested VOC reduction formulary guide, to improve products sold in California and reduce the level of petroleum products released into our environment. Multiple formulas are suggested with d-limonene (a citrus terpene). (data released 3/18/04 as examples of formulas that comply with ARB proposed VOC regulations)

While the overall goal of this draft report is well intentioned, there are several incorrect statements made regarding d-limonene and terpenes that are opinion, only based on excerpts from selected literature. These opinions are in direct opposition to other Federal and California rulings and agencies:

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1. Citrus terpenes and d-limonene are NOT Toxic Air Pollutants:

In two tables (Pages 17 and 124) reference is made to terpenes being Toxic Air Pollutants. This report defines TAPs as one of the following; pollutants identified as Toxic Air Contaminants (TACs) by ARB, identified as Proposition 65, or criteria air pollutants. Terpenes and d-limonene are NOT on the TAC list. Citrus terpenes and d-limonene are NOT on the California Governor's Proposition 65 List. Terpenes and d-limonene are NOT criteria air pollutants. We ask you remove these incorrect references from your report.

2. Citrus terpenes and d-limonene are NOT carcinogens: This draft report states:

"Reformulation of other products, such as cleaning agents to remove terpenes could go far to reduce irritant and carcinogenic effects." (Pages 18, 124-125) This is a false statement. The suggestion that any cancer risk has been associated with d-limonene is simply wrong and CANNOT be supported with any scientific evidence. Terpenes and d-limonene are not on the California Governor's Proposition 65 List and are not currently under review to be on the California Proposition 65 List. Again this report makes statements in direct opposition to an existing California report. d-Limonene IS NOT listed as a carcinogen by the National Toxicology Program (NTP) or the International Agency for Research on Cancer (IARC). We ask you remove these incorrect references from your report.

3. Citrus terpenes and d-limonene are NOT indoor air pollutants:

Our products are used extensively by industry and have been closely monitored in a variety of indoor environments. No evidence exists to support the unwarranted claims that citrus terpenes, such as d-limonene, can be characterized as "indoor air pollutants" or "irritant chemicals" (Pages 5, 14, 30-31, 34, 35, and 54). No OSHA, NIOSH or ACGIH limits have been published for exposures to d-limonene.

This draft report also states that "Pollutants with reactive double bonds such as terpenes and alkenes react with ozone and nitrogen oxides to produce airway irritation similar to that of formaldehyde. Fan et al. (2003) confirmed the reaction of ozone with d-limonene and ozone with α -pinene to generate formaldehyde and ultrafine particles." (Page 35) This statement alone is extremely MISLEADING to the true content of the research. **It is important to include the conclusions of cited literature rather than selected statements.** Fan et al (2003) go on to conclude :

"Alkenes that exhibit high ozone reactivities are commonly present indoors. **Outdoor ozone can enter these indoor settings, initiating the production of potentially irritating oxidized compounds** that are not only present in the gas phase but also contribute to the growth of fine particles. To reduce the production of such undesirable products, it is prudent to limit the use of products that emit high-reactivity alkenes during episodes when outdoor ozone levels are elevated. However given the practical difficulties associated with such changes in established use patterns, **it is even more crucial to reduce outdoor ozone levels or to minimize the unimpeded penetration of ozone from outdoors.**"¹

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The author also states, "although the compounds present in the mixture are among some of the more commonly observed compounds in indoor air, the concentrations employed in this study tend to be much higher than those observed in nonindustrial indoor environments"¹

The clear conclusion that can be drawn from the work of Fan et al, is that indoor chemical reactions between ozone and VOC's are OZONE LIMITED. As demonstrated by Fan's VOC study, no reactions/particulate formation occurred with the 23 VOCs studied in the absence of ozone. Removing specific VOC's from indoor air solves nothing because there is abundant biogenic VOC's (specifically terpenes) in indoor air. This is due to the fact that both humans and plant life emit isoprene and other VOC's. Therefore as long as the elevated ozone levels are present the reactions will occur that generates particulate and irritants. Fan states it best in his conclusion, "...it is even more crucial to reduce outdoor ozone levels".

We ask you remove the incorrect references from your report(Pages 5, 14, 30-31, 34, and 54). The statements made on Page 35 citing literature should be removed, or the author's conclusions and qualifiers (that we have shown above) should be added.

4. Citrus terpenes and d-limonene are NOT irritants:

Throughout the report terpenes are identified as irritants. Then the report states "Terpenes are associated with irritation, though it is believed that the irritant chemicals are a product of the reaction of terpenes with oxidants (Wilkins et al., 2001; Weschler and Shields, 1997) (Page 34)

The scientific community has concluded that **IF** any irritation is observed, it is from the oxidized form of d-limonene. Karlberg, et al have reported this based upon studies that controlled the oxidation of the d-limonene. There were no sensitization issues when the oxidized form was not present. The reactions that were observed were similar to allergic reactions in that the extent and severity of the reaction varied from individual to individual. **Also not all members of the test group reacted to the oxidized form of d-limonene.**²

It is important to include the conclusions of cited literature rather than selected statements. In the paper cited by the draft report, Wilkins concludes the following:

"An intriguing question, which is partly the basis for the investigation, is whether these oxidative processes contribute significantly to human airway irritation during periods of **elevated indoor O₃** (and/or NO₂) concentrations and/or **in crowded buildings with low air exchange rates** (elevated isoprene and other reactive olefin concentrations). The concentration of isoprene in the lung is low (25-200 ppb) and somewhat lower in an occupied room (~ 20 ppb). At these low concentrations, the oxidation processes are much slower, but it is possible that during extended exposure they could contribute to the reported airway irritation. Aldehydes have been identified in bronchoalveolar lavage of rats exposed to 0.5-10 ppm ozone undoubtedly from the oxidation of unsaturated fatty acids. These authors suggested that oxidation intermediates (ozonides, hydroxyl-hydroperoxides) might be involved in the inflammatory process.

It is also interesting the blood levels of isoprene in humans have been reported to be 1-5 mg/m³ whereas the other mammals investigated had blood levels of < 70 µg/m³, suggesting that some aspects of terpene biosynthesis in humans are unique.

The upper airway irritation observed in mice exposed to isoprene/oxidant mixtures could not be explained by concentrations of residual reactants and reaction products identified by some

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conventional sampling/analytic procedures. It is likely that strongly irritating, unstable products are responsible for the unexplained airway irritation. **The practical and rather ironic implication of these observations may be that humans themselves produce one of the compounds, which may contribute to upper airway irritation indoors.**³

Citrus terpenes and d-limonene should not be identified as irritants in your report.

This draft report is not the place for ARB to present theories as conclusions. ARB should not allow misleading statements to remain, as they only cast doubt on the accuracy of the report. Failure to correct these statements would be irresponsible on the part of the Board.

In March we gave a presentation to ARB Stationary Source Division staff about citrus by-products relative to VOCs. We welcome the opportunity to repeat this presentation and discuss any concerns regarding citrus terpenes. If you have questions please direct them to me, or our legal counsel Livingston and Mattesich in Sacramento. Thank you for the opportunity to comment on this report.

Respectfully submitted,

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Vice President of Product Development
Florida Chemical Company, Inc.

Jon Leonard
Director of R & D
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cc: Jim Mattesich, Livingston and Mattesich

¹ Fan Z, Liyo P, Weschler C, Fiedler N, Kipen H, and Zhang J, 2003. Ozone-initiated reactions with mixtures of volatile organic compounds under simulated indoor conditions. *Environmental Science and Technology* 37:1811-1827.

² Karlberg, A.T. *et al*; Animal experiments on the allergenicity of d-limonene--the citrus solvent, *Ann. Occup. Hyg.* 35: 419-426 (1991).

Karlberg, A.T. *et al*; Air Oxidation of d-limonene (the citrus solvent) creates potent allergens, *Contact Dermatitis*, 26: 332-340 (1992).

³ Wilkens CK, Clausen PA, Wolkoff P, Larsen ST, Hammer M, Larsen K, Hansen V, and Nielsen GD, 2001. Formation of strong airway irritants in mixtures of isoprene/ozone and isoprene/ozone/nitrogen dioxide. *Environ Health Perspect* 109(9): 937-941.