

**“Keratin-Based”
Hair Smoothing Products
And the Presence of Formaldehyde**

**Oregon OSHA
A Division of the Oregon Department of Consumer and Business Services**

**and CROET
at Oregon Health & Sciences University**

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Executive Summary

Background

Earlier this year, a stylist at a Portland area hair salon contacted staff at the Center for Research in Occupational and Environmental Toxicology (CROET) at the Oregon Health Sciences University (OHSU) as a result of difficulty breathing, nose bleeds and eye irritation when using a popular hair smoothing product. The salon had discontinued the use of the product due to these adverse effects. The product, when used as directed, is combed in, blow dried and heated with flat irons during the treatment process. In evaluating the issue, CROET noted that the material safety data sheet (MSDS) accompanying the product listed no hazardous ingredients or impurities. The MSDS also indicated no respiratory hazards or related precautions. The container did not include chemical ingredients on its label.

CROET asked for Oregon OSHA's assistance in collecting a sample and determining the content of the product, known as Brazilian Blowout Solution. The Oregon OSHA laboratory analyzed the sample using five different test methods, four of which provide "quantitative" results while the fifth simply indicates whether formaldehyde is present at detectable levels. Each of the five separate analyses concluded that formaldehyde was present well above regulated levels, with the quantitative methods producing respective results ranging from 6.3 to 10.6 percent. In analyzing samples of a newer "formaldehyde free" version of the product, Oregon OSHA's laboratory found it contained roughly 8.5 percent formaldehyde.

In response to these findings, and based not only on the lack of information available to stylists on the hazards but also on the newer product's prominent label declaration and marketing of the product as "formaldehyde free," CROET posted an advisory on its website and Oregon OSHA began an enforcement initiative allowing it to obtain a significant number of additional samples from Oregon salons, as well as to conduct air monitoring in addition to the monitoring conducted at the request of several salons. That laboratory analysis found formaldehyde in all the Brazilian Blowout samples analyzed as well as in several other products, to varying degrees.

Signs, Symptoms and Effects of Formaldehyde Exposure

The irritant effects of formaldehyde are well documented, with reports of eye, nose and throat irritation, loss of sense of smell, increased upper respiratory disease, dry and sore throats, respiratory tract irritation, cough, chest pain, shortness of breath and wheezing. The National Institute for Occupational Safety and Health (NIOSH) cites many reports of primary skin irritation and allergic dermatitis as a result of skin contact with water solutions of formaldehyde.

Both the Environmental Protection Agency and the federal Occupational Safety and Health Administration classify formaldehyde as a suspected human carcinogen because of links to nasal cancer and leukemia, while NIOSH and the International Agency for Research on Cancer list it as a known human carcinogen.

Formaldehyde and Methylene Glycol

Oregon OSHA and CROET have concluded that it is scientifically correct to measure the "formaldehyde content" of a solution without excluding that portion of the formaldehyde that has reacted with the water to form "methylene glycol." While discussions about the value of such a distinction may continue, the fact remains that existing workplace health regulations and

widespread practice in protecting workers from dangerous chemicals has considered and continues to consider formaldehyde mixed with water to be appropriately described as “formaldehyde in solution.” The hazards posed by these products remain the same regardless of the name used to describe them. The Formaldehyde Standard enforced by both federal OSHA and Oregon OSHA applies to formaldehyde in all of its forms and specifically includes several other terms, including “methylene glycol.”

Overview of Sample Results

A total of 105 samples of various hair-smoothing products were taken from 54 Oregon salons. Of these, 37 samples came from bottles of the Brazilian Blowout Acai Professional Smoothing Solution, labeled “formaldehyde free.” The formaldehyde content of these samples ranged from 6.8 percent to 11.8 percent and averaged more than 8 percent. An additional 19 of the samples were of Brazilian Blowout Solution (not labeled “formaldehyde free” but does not mention formaldehyde on its packaging or material safety data sheet). The formaldehyde content of these samples ranged from 6.4 to 10.8 percent and averaged approximately eight percent.

In addition to the Brazilian Blowout products, a limited number of samples also were taken of several other hair smoothing products. With three exceptions, all the other products tested at less than 2.5 percent formaldehyde, although several of them were above the 0.1 percent threshold of the OSHA Formaldehyde Standard.

Oregon OSHA also conducted air monitoring during treatments using the Brazilian Blowout smoothing product at seven different salons where a single treatment was conducted over the course of the day. The 8-hour average exposures ranged from a low of 0.006 parts per million (ppm) to 0.33 ppm. These compare to a permissible exposure limit of 0.75 ppm. Although it was not exceeded for any of these stylists, it should be noted that multiple treatments would increase the daily average significantly.

During its air monitoring, Oregon OSHA also found short-term exposures ranging from a high of 0.11 for one stylist to a high of 1.88 ppm for another. These compare to a short-term exposure limit of 2.0 ppm. The limit was not exceeded, although the highest short-term exposure represents 94 percent of the short-term limit.

Oregon OSHA and CROET also note that the recommended exposure limits of both the American Conference of Government Industrial Hygienists (ACGIH) and the National Institute for Occupational Safety and Health (NIOSH) are much more protective than the regulatory levels adopted by OSHA. Almost all the sample results in these cases exceeded both the ACGIH and NIOSH recommended levels.

Conclusion

Oregon OSHA and CROET have concluded that there are meaningful risks to salon workers when they are confronted with these hair smoothing products. Effective control of those risks depends upon accurate information regarding the potential hazards and the control measures available, which in turn begins with an accurate understanding of the ingredients and the potential harm they may cause.

In conjunction with this report, Oregon OSHA is advising Oregon salons and stylists that hair-smoothing treatments – particularly those generally referred to as “Keratin-based treatments” –

should generally be treated as formaldehyde-containing products and the requirements of the OSHA Formaldehyde Standard must be followed when there are employees under the Oregon Safe Employment Act (OSEA). Further, employers should be advised that any product that contains “methylene glycol” will continue to be treated as a formaldehyde-containing product under the OSEA.

Authors

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McCarthy has coauthored the following peer-reviewed papers:

- P.K. Freeman and Kermit McCarthy, "Photochemistry of oxime carbamates; Phototransformations of aldicarb". *Journal of Agricultural and Food Chemistry*, 1984, 32, 875.
- J.H. Fellman, E.S. Roth, N.A. Avedovech and K.D. McCarthy, "Mammalian hypotaurine amino transferase: isethionate product". *Life Sciences*, 1980, 27 (21), 1999.
- J.H. Fellman, E.S. Roth, N.A. Avedovech and K.D. McCarthy, "The metabolism of taurine to isethionate". *Archives of Biochemistry and Biophysics*, 1980, 204 (2), 560
- Marija Janko, Kermit McCarthy, Michael Fajer and John Van Raalte, "Occupational Exposure to 1,6-Hexamethylene Diisocyanate-Based Polyisocyanates in the State of Oregon, 1980-1990". *American Industrial Hygiene Association Journal*, 1992, 53, 331.
- Marija Janko, Kermit McCarthy, et al., "Personal monitoring for formaldehyde using activated 13x molecular sieve tube". *Journal of Applied Industrial Hygiene*, 1987, 3.

McCarthy, a member of the Pacific Northwest Section of the American Industrial Hygiene Association, also has been a frequent presenter at the Northwest Occupational Health Conference and at other venues. A limited sample of his presentation topics includes the following:

- "Analysis of Wood Preservatives," to the Northwest Occupational Health Conference
- "Current Issues in Ozone Analysis," to the Northwest Occupational Health Conference
- "Methyl Mercaptan Analysis," to the Northwest Occupational Health Conference
- "Analysis of Isocyanates," to the Northwest Occupational Health Conference
- "The Effect of Blank Values on the Detection Limit of Formaldehyde," to the Northwest Occupational Health Conference
- "Basic Chemistry" for the CIH/CSP Preparation Class at the Oregon Governor's Conference

²Mr. McLaughlin began his career in industrial hygiene with the US Air Force in 1987, and joined Oregon OSHA in 1991, working first as a Health Compliance Officer. He became part of the Technical Section in 1996 and has worked on writing and revising rules, publications, interpretations, and fact sheets. He provides technical assistance to Oregon OSHA field staff as well as employers.

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Reviewers

In addition to the listed authors, a number of CROET and Oregon OSHA staff helped to prepare and review this report. Without their efforts, this report could not have been completed in the relatively short time period available. In addition, CROET and Oregon OSHA thank those chemistry and toxicology experts listed below, who agreed to review drafts of the report specifically in relation to the discussion of the chemistry and toxicology of formaldehyde in an unusually short time frame. Their courtesy and assistance are greatly appreciated by the authors.

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- **Russell L. Dills, PhD.** Dr. Dills has been a research scientist in the University of Washington's Department of Environmental and Occupational Health Sciences since 1988 and has been the Director of the UW's Environmental Health Laboratories and Trace Organic Analytical Center since 2005. He received his PhD in Toxicology from the University of Kansas Medical Center in 1986. He has Bachelor of Science degrees from the University of Washington in both Chemistry and Biology. Dr. Dills has published extensively in peer-reviewed literature, having authored or co-authored more than 40 articles in publications such as *Analytical Chemistry*, *The Journal of Pharmacology*, *The Journal of Chromatography*, *The Journal of Occupational Health*, and *Chemical Research in Toxicology*. Many of these articles relate specifically to the analysis of workplace chemical samples, a subject on which he also has presented frequently.
- **Michael M. Haley, PhD.** Dr. Haley is Head of the Chemistry Department at the University of Oregon, where he is a professor of organic, organometallic, and materials chemistry. He is a member of the University's Materials Science Institute, an interdisciplinary State Center of Excellence. Dr. Haley received his PhD and Bachelor of Arts from Rice University. Dr. Haley has received numerous awards for excellence in both teaching and research. Dr. Haley has published in a number of peer-reviewed journals and is the author or co-author of more than 100 articles in publications such as *The Journal of the American Chemical Society*, *The Journal of Organic Chemistry*, *The Journal of Physical Chemistry*, and *Organometallics*.
- **Thomas M. Harris, PhD.** Dr. Harris is Centennial Professor, Emeritus and a Research Professor at Vanderbilt University. Dr. Harris received his PhD in Organic Chemistry from Duke University and his Bachelor of Science in Chemistry from the University of Rochester. His career in Vanderbilt's Department of Chemistry began in 1964 and includes ancillary appointments, among them 28 years in Vanderbilt's Center for Environmental Toxicology, including 19 years as Associate Director of the Center. Among his

rules, as well as providing technical guidance documents and other materials. Ms. Schuster was previously employed by Federal OSHA in Portland and Washington, D.C., where she managed the regulatory impact analysis of OSHA standards. While at Federal OSHA, Ms. Schuster was a part of the standards development team that adopted the 1992 formaldehyde standard. A member of the American Society of Safety Engineers, Ms. Schuster has both a Masters of Business Administration and a Bachelor of Science in Psychology from Portland State University. ⁶Mr. Wood has been the Administrator of Oregon OSHA since 2005. Prior to that, he worked for more than 10 years as the Senior Program Manager for WISHA Policy & Technical Services at the Washington State Department of Labor and Industries and spent eight months as the Acting Assistant Director for WISHA Services. He is a 1983 graduate of Gonzaga University, with a Bachelor of Arts in English and Political Science, and was certified by the Board of Certified Safety Professionals in 2003. Mr. Wood is a professional member of the American Society of Safety Engineers and an affiliate member of the American Industrial Hygiene Association.

many honors are several years on the Editorial Advisory Board of *Chemical Research in Toxicology* and the 1993 Earl Sutherland Award for Excellence in Research. Dr. Harris has published extensively in peer-reviewed journals and is the author or co-author of more than 300 articles in journals such as *The Journal of the American Chemical Society*, *The Journal of Organic Chemistry*, *Biochemistry*, and *Chemical Research in Toxicology*.

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Background and History

Although the discussion of formaldehyde in relation to hair straightening and smoothing treatments has been going on within the industry for some time, the direct involvement of the State of Oregon from a workplace health and safety perspective began earlier this year.

Staff at the Center for Research in Occupational and Environmental Toxicology (CROET) at the Oregon Health Sciences University (OHSU) were contacted by a local Oregon salon regarding a product used in the salon that appeared to cause difficulty breathing, nosebleeds and eye irritation in stylists using the product as directed. The salon had discontinued the use of the product due to these adverse effects. The product, named Brazilian Blowout Solution,⁷ is used as a hair smoother and is applied to the hair, which is then heated with flat irons during the treatment process. In evaluating the issue, CROET noted that the material safety data sheet (MSDS) accompanying the product listed no hazardous ingredients or impurities. The MSDS further identified no respiratory hazards or precautions. No chemical ingredients label appears on the container.

In an effort to identify a potential source for the reported symptoms, CROET requested consultative services from the Occupational Safety and Health Division of the Oregon Department of Consumer and Business Services, generally known as “Oregon OSHA.” CROET staff delivered the original container to Oregon OSHA, and an Oregon OSHA industrial hygiene consultant took a sample of the contents using standard sampling protocols. The sample was then delivered to Oregon OSHA’s own accredited laboratory for analysis.

Test results demonstrated that the product contained 4.8 percent formaldehyde by weight, well beyond levels that could accurately be described as “incidental” or “trace” levels of the product.⁸ The product also was found to contain methanol, ethanol, 2-hydroxyethyl methacrylate, and hexadecanol.

CROET also noted that the symptoms by the stylists who raised the issue are consistent with formaldehyde exposure.

As a result of these initial results, and because of the lack of readily available information regarding the hazards of the product, CROET issued a notice on its “emerging issues and alerts” web page on September 16, 2010.⁹

In researching the issue, CROET had become aware of previous industry reports of formaldehyde in similar products and noted that the company had begun marketing a “formaldehyde free” product named the Acai Professional Smoothing Solution.¹⁰ Before

⁷The salon provided CROET with documentation indicating that the specific product had been shipped to the salon by Brazilian Blowout on August 31, 2009.

⁸Formaldehyde exists at trace levels in many substances. With regard to the amount of formaldehyde in these products, it may be worthwhile to note that solutions for the preservation of laboratory specimens typically contain 10 percent formalin. Formalin itself is a solution that contains 37 percent formaldehyde. In other words, the amount of formaldehyde present in a typical solution sold to schools, hospitals and other laboratories for the preservation of tissue is roughly 3.7 percent by weight. See, for example, <http://www.sciencestuff.com/prod/Chem-Rgnets/C1771>.

⁹This alert and CROET’s subsequent alerts can be accessed on the CROET web page. The alert is found at <http://www.ohsu.edu/xd/research/centers-institutes/croet/emerging-issues-and-alerts.cfm>.

¹⁰It is not clear exactly how the Acai Professional Smoothing Solution differs from the prior product. However, the company indicated on its Facebook page on October 4, 2010, that “Our old formula contained glutaraldehyde. We October 29, 2010

recommending the new, apparently reformulated product to the salon as a solution to the problem, CROET arranged to obtain a sample of the new product from a different salon. Again, CROET brought the original bottle to an Oregon OSHA industrial hygiene consultant, who again took a sample and provided it to the laboratory for analysis.¹¹

The Oregon OSHA laboratory analyzed the sample using five different test methods, four of which provide “quantitative” results while the fifth simply indicates whether formaldehyde is present at detectable levels. Each of the five separate analyses concluded that formaldehyde was present well above regulated levels, with the quantitative methods producing respective results of 10.6 percent, 6.3 percent, 10.6 percent and 10.4 percent.¹²

In response to these findings, and based not only on the lack of information on the hazards but also on the prominent label declaration and marketing of the product as “formaldehyde free,” CROET issued an updated advisory on September 24, 2010. In order to ensure that the results were not the result of tampering with the product, Oregon OSHA contacted a salon identified from the Brazilian Blowout website to ask for a sample of the product. An Oregon OSHA staffer went to the salon and obtained a sample directly from a bottle of the Acai Professional Smoothing Solution.¹³ The laboratory’s analyses of this product sample determined that formaldehyde was present using four different methods, and the three quantitative methods identified the concentration of formaldehyde by weight respectively at 8.4 percent, 8.6 percent and 8.7 percent.

Also on October 5, 2010, Oregon OSHA began an enforcement initiative allowing it to obtain directly from Oregon salons a significant number of additional samples of products, including products from other manufacturers. In addition, the initiative provided the opportunity for air monitoring in addition to monitoring conducted at the request of several salons. The conclusions reached as a result of all the samples gathered, including those gathered as a result of this enforcement emphasis, are discussed at length elsewhere in the document. However, laboratory analysis found formaldehyde in all the Brazilian Blowout product samples analyzed (as well as in several other products, to varying degrees).

reformulated in October of 2009 to become hyde free” and stated on October 5, 2010, “Our solution changed in October of 2009. We used to have glutaraldehyde in our solution but our reformulation does not contain a "hyde" of any sort.”

¹¹In the case of the second bottle, the salon provided CROET with documentation indicating that the specific product had been shipped by the company on August 12, 2010. No samples were received by Oregon OSHA from any source in unmarked bottles.

¹²Of the four methods, Oregon OSHA’s laboratory has generally considered the method resulting in the 6.3 percent result to be the least reliable in determining the amount of formaldehyde present. This method is intended to analyze samples in the range of 0.1 to 2 percent formaldehyde. At more than 2 percent formaldehyde, the endpoint is difficult to determine.

¹³The bottle, like the other bottles tested, was in use and had therefore been opened. On the same visit, at the request of the salon, Oregon OSHA also obtained samples of two other hair smoothing treatments. Subsequent analysis also found formaldehyde in those samples, although at somewhat lower levels (ranging between 0.97 and 1.2 percent for one product and between 2.1 and 2.2 percent for the other). These results are included in the discussion of the laboratory analyses found in a later section of this document.

On October 8, 2010, Oregon OSHA issued an advisory suggesting “continued caution by salon workers” and noting that the federal OSHA standard applies not only to gaseous formaldehyde but also to formaldehyde in solution, including methylene glycol.¹⁴

The purpose of the present report is to provide a discussion of the issues raised and the results of Oregon OSHA’s laboratory tests as they relate to Oregon employers and Oregon workers. For the reasons discussed at greater length in the remainder of this document, Oregon OSHA and CROET have concluded that there are meaningful risks to salon workers when they are confronted with these hair smoothing products. Effective control of those risks depends upon accurate information regarding the potential hazards and the control measures available, which begins with an accurate understanding of the ingredients and the potential harm they may cause.

¹⁴The advisory can be found at http://www.cbs.state.or.us/osh/admin/newsrelease/2010/nr2010_25.pdf. The suggestion that formaldehyde effectively ceases to be appropriately referenced as formaldehyde when it is dissolved in water is dealt with at some length in other portions of this document.

Signs, Symptoms and Effects of Formaldehyde Exposure¹⁵

The majority of formaldehyde exposures occur by inhalation or through skin and eye contact. Most people can detect the odor of formaldehyde at concentrations between 0.5 and 1.0 parts per million. Those people who become sensitized to formaldehyde may experience headaches and minor eye and airway irritation even at relatively low levels.

The irritant effects of formaldehyde are well documented, with reports of eye, nose and throat irritation, loss of sense of smell, increased upper respiratory disease, dry and sore throats, respiratory tract irritation, cough, chest pain, shortness of breath and wheezing. The National Institute for Occupational Safety and Health (NIOSH) cites many reports of primary skin irritation and allergic dermatitis as a result of skin contact with water solutions of formaldehyde.

The American Conference of Industrial Hygienists (ACGIH) recognizes formaldehyde as a sensitizer, based on the reports of allergic reactions/sensitizations following occupational and non-occupational exposures. Sensitizers not only can cause allergic reactions in at least some individuals, but they also increase the risk that exposed individuals will react to the substance in the future, perhaps at much lower exposures. In the case of formaldehyde, the widespread exposure to the product at low levels heightens the concerns with regard to sensitization.

ACGIH notes that “there is a substantial portion of the population, comprising up to 20%, for whom airborne formaldehyde at concentrations on the order of 0.25 to 0.5 ppm is troublesome” and that “it is plausible that a similar proportion (10% to 20%) who are more responsive, may react acutely to formaldehyde at very low concentrations <0.25 ppm.” ACGIH further states that in consideration of these reports, “individuals who may already be sensitized or otherwise unusually responsive to formaldehyde may not be adequately protected from adverse health effects caused by formaldehyde exposures at or below the recommended threshold limit values, TLV (ceiling) of 0.3 ppm.”

Adverse effects on the central nervous system such as increased headaches, depression, mood changes, insomnia, irritability, attention deficit, and impairment of dexterity, memory and equilibrium have been reported to result from long-term exposure.

Although the evidence in humans has been questioned by some in industry, both the Environmental Protection Agency and the federal Occupational Safety and Health Administration regard formaldehyde as a possible human carcinogen and regulate it accordingly. The best documented risks involve nasal cancer.

There have been reports of menstrual disorders in women occupationally exposed to formaldehyde, but they are controversial. Formaldehyde has not been proven to cause birth defects in animals and is probably not likely to cause birth defects in humans at occupationally permissible levels. However, special consideration regarding the exposure of pregnant women is warranted since formaldehyde has been shown to damage DNA.

¹⁵The material in this section is based upon guidance provided in *Documentation of the Threshold Limit Values and Biological Exposure Indices, 7th Edition*, published by the ACGIH and in “Medical Management Guidelines for Formaldehyde,” published by the Agency for Toxic Substances & Disease Registry, United States Department of Health and Human Services.

CROET has received numerous phone calls and emails from stylists from around the United States since first posting an alert on the hair product on September 16, 2010. Many of the stylists reported health symptoms associated with the use of this product at work. The health symptoms reported include the following: burning of eyes and throat, watering of eyes, dry mouth, loss of smell, headache and a feeling of “grogginess,” malaise, shortness of breath and breathing problems, a diagnosis of epiglottitis attributed by the stylist to their use of the product, fingertip numbness, and dermatitis. Some of these effects were also reported to have been experienced by the stylists’ clients. CROET also received emails from persons who report hair loss after having the treatment. Oregon OSHA has received similar, although generally less detailed, reports from individuals who have contacted the agency as a result of recent media coverage.

Formaldehyde and Methylene Glycol

Overview

The question has been raised as to whether it is scientifically incorrect to measure the “formaldehyde content” of a solution without excluding that portion of the formaldehyde that has reacted with the water to form “methylene glycol.” Based on an understanding of both the chemistry and the toxicology involved, CROET and Oregon OSHA have concluded that it is indeed appropriate to refer to both the hydrated and the non-hydrated formaldehyde as formaldehyde, finding the distinction to be of no relevance in the context of worker protection.

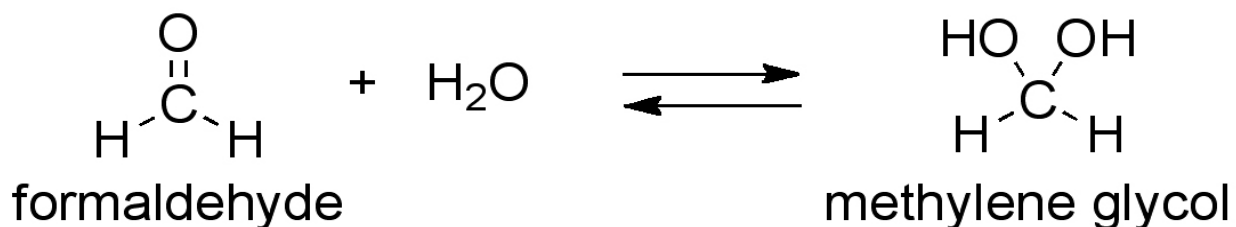
The rigid distinction between gaseous formaldehyde and hydrated formaldehyde is widely disregarded throughout the commercial chemical industry, as well as throughout the general practice of chemistry and, in particular, the practice of toxicology. Indeed, any dictionary definition of the term “formalin” is likely to define it as “formaldehyde in solution.” Even advocates for limiting the use of the term “formaldehyde” to refer to gaseous formaldehyde alone acknowledge that their position is widely disregarded, although they mistakenly conclude that this disregard is the result of a failure of researchers, analytical chemists, toxicologists and other professionals to understand the basic chemistry involved.

While the argument about the value of such a distinction may continue, the fact remains that existing workplace health regulations and widespread practice in protecting workers from dangerous chemicals has considered and continues to consider formaldehyde mixed with water to be appropriately described as “formaldehyde in solution.”

Toxic actions of formaldehyde occur after gaseous formaldehyde has become dissolved in water – free gaseous formaldehyde does not exist in cells – and to interact with cells covered with a film of water, such as the eyes, the formaldehyde must first dissolve. An example of the toxic effects of formaldehyde solutions can be seen in the changes tissues go through in the practice of embalming. Solutions used for tissue preservation and other purposes are, as noted below, routinely sold as “formaldehyde.” In all such cases, the majority of the formaldehyde reacts with the water, as described in the following section, but remains potent.

Formaldehyde in solution

When formaldehyde is dissolved in water a large percentage is hydrated to form a *gem*-diol and a very small percentage is left as gaseous formaldehyde.¹⁶



¹⁶See, for example, Winkelman et al, “Kinetics and Chemical Equilibrium of the Hydration of Formaldehyde,” *Chemical Engineering Science* 57 (2002) p. 4067: “Because formaldehyde is unstable in its pure, gaseous state it is usually produced as an aqueous solution. In such a solution, formaldehyde is almost completely hydrated to methylene glycol.”

Although most of the gaseous formaldehyde in the solution therefore becomes hydrated (methylene glycol), this equilibrium between the gaseous and hydrated formaldehyde remains in flux. In mere fractions of a second, gaseous formaldehyde is hydrated and hydrated formaldehyde returns to the gaseous state. And the equilibrium is “rebalanced” every time that gaseous formaldehyde is used or released into the air. As a result, the hydrated formaldehyde portion of the solution effectively becomes a reservoir of gaseous formaldehyde.

Solutions of formaldehyde left in the open air release gaseous formaldehyde. As this takes place, hydrated formaldehyde in the solution is dehydrated, producing (and releasing) more gaseous formaldehyde, and the overall concentration of formaldehyde (both gaseous and hydrated) in the solution is reduced. This dynamic process continues, therefore, not until the original amount of gaseous formaldehyde alone has been “used up.” Instead, under certain conditions it will continue until the hydrated portion of the solution has been depleted.¹⁷

The rate of release of gaseous formaldehyde and the resultant depletion in solution is increased with agitation or heat. The gaseous formaldehyde in the solution reacts with chemicals, human hair or tissue with the same consequence. The reaction uses up the available gaseous formaldehyde, which in turn is replenished from the reservoir of hydrated formaldehyde available in the solution. For this reason, the hazards associated with the use of a solution of formaldehyde are the same as the hazards of gaseous formaldehyde since the solution so readily releases gaseous formaldehyde. And describing the solution as containing only the amount of gaseous formaldehyde in the solution distorts the risks and dramatically understates the amount of formaldehyde readily available in the solution.

It is the recognition of that reality that causes industrial chemists and toxicologists (as well as those teaching high school and college chemistry) to refer to the solutions as “containing” formaldehyde. The formaldehyde can be placed in solution – and the chemical can be removed from solution. The fact that most of it temporarily changes chemical form while it is in solution does not change the reality in any meaningful fashion. A somewhat similar process occurs with saline solution – but manufacturers and users of saline solution quite correctly describe the solution as containing “salt.”¹⁸

References in Scientific Literature and the Industry “Marketplace”

The International Union of Pure and Applied Chemists (IUPAC) calls the *gem*-diol formed (the hydrated form of formaldehyde) methanediol. One synonym for this is indeed methylene glycol. The IUPAC is the international group that gives chemicals their official names. In practice, these terms are rarely used. The international chemical community often refers to the substance

¹⁷Although not an issue in relation the products in question, formaldehyde also appears in solid forms. Trioxane is a trimer of formaldehyde and para-formaldehyde is a polymer of formaldehyde. Formaldehyde gas is liberated from trioxane and para-formaldehyde when heated (cracked).

¹⁸Although salt, known chemically as “sodium chloride” (NaCl) is added to water to create saline solution, most of the sodium chloride separates when the salt is dissolved in water. As a result, the saline solution contains separate sodium and chloride ions. When the water is removed by heat or evaporation, however, the chemical bond is restored and the sodium chloride reforms. In spite of this transitory chemical reaction, manufacturers of saline solution routinely describe the solution as containing a certain percentage of “salt” or of sodium chloride.

as formaldehyde in solution or formalin.¹⁹ In addition, texts on chemistry and toxicology routinely refer to formaldehyde as existing in solution.²⁰

The authoritative guide *Patty's Toxicology*, in discussing formaldehyde, lists both formalin and methylene glycol as among the many synonyms for formaldehyde.²¹

Chemical companies offering chemicals for sale do not list methanediol or methylene glycol in their catalogs. They list formaldehyde solutions or formalin. Frequently, a search for “formaldehyde” will find few if any references to anything other than formaldehyde in solution.²² If methylene glycol is not appropriately described as formaldehyde in solution, it would mean that these companies are in error when they claim to sell formaldehyde – and it would mean that the formaldehyde solutions they sell should all be appropriately labeled “formaldehyde free.” To the contrary, the bottles, material safety data sheets and certificates of analysis for these products do not list “percent methanediol” or “percent methylene glycol.” They list “percent formaldehyde.”

¹⁹See, for example, the following resources that refer to “formaldehyde in solution:”

- the NIOSH Pocket Guide to Chemical Hazards at <http://www.cdc.gov/niosh/npg/npgd0294.html>;
- the International Chemical Safety Pocket Cards published by NIOSH and several international partners at <http://www.cdc.gov/niosh/ipcsneng/neng0695.html>;
- the Agency for Toxic Substances and Disease Registry (ATSDR) Toxicological Profile at <http://www.atsdr.cdc.gov/toxprofiles/tp111-c3.pdf>;
- the Hazardous Substance Data Bank of the United States National Library of Medicine (NLM) at http://hazmap.nlm.nih.gov/cgi-bin/hazmap_generic?tbl=TblAgents&id=760;
- published monograph of the International Agency for Research on Cancer (IARC) of the World Health Organization (WHO) at <http://monographs.iarc.fr/ENG/Monographs/vol88/mono88-6.pdf>.

²⁰See, for example, the following references (the apparent inconsistency regarding the amount of formaldehyde in standard full-strength formalin is that such solutions are 37 percent formaldehyde by weight, but 40 percent formaldehyde by volume):

- *Organic Chemistry*, by L.G. Wade, Jr. (1999), 4th edition, published by Prentice-Hall, Inc., discusses the issue on pages 789-790. Although the graphics on page 790 clearly acknowledge the change in chemical structure, the text on page 789 includes the following statement: “Formaldehyde is a gas at room temperature, so it is often stored and used as a 40 percent aqueous solution called *formalin*.”
- *Fundamentals of General, Organic, and Biological Chemistry*, by John McMurry and Mary E. Castellion (2006), 4th edition, published by Pearson Education, Inc. discusses formaldehyde on pages 449-450, including the statement “Formaldehyde is commonly sold as a 37%...aqueous solution under the name *formalin*.” The text’s discussion of the general relationship between dose and toxicity on page 455 also refers to “formaldehyde in solution.”
- *Toxics A to Z: A Guide to Everyday Pollution Hazards*, by John Harte, Cheryl Holdren, Richard Schneider and Christine Shirley (1991), published by the University of California, includes a discussion of formaldehyde on pages 318 through 321. It includes following observation on page 318: “Generally sold in alcohol solutions, formaldehyde retains its odor and ability to irritate eyes and mucous membranes. Any biology student who has dissected a frog or a worm is familiar with formaldehyde in the form of the preservative formalin, a clear, watery solution having a characteristic pungent odor.”

²¹Eula Bingham, et al, ed. *Patty's Toxicology*, 5th edition, p. 979.

²²See, for example, the following:

- A search for “formaldehyde” at the Science Kit & Boreal Laboratories web site identified six products, all identified as “solutions” of formaldehyde (see <http://sciencekit.com>); a search for “methylene glycol” failed to identify any products.
- A search for “formaldehyde” at VWR International found dozens of solutions containing formaldehyde (see <https://www.vwrsp.com/>).

In analyzing and discussing methods for determining the formaldehyde content of air samples, the National Institute for Occupational Safety and Health and other organizations routinely refer to “formaldehyde solutions” or “aqueous formaldehyde.”²³ Such methods include the aqueous formaldehyde in such solutions – not just the small amount that exists in gaseous form – when determining the amount of “free formaldehyde” present in the solution.²⁴

In its congressionally-mandated *Report on Carcinogens*, the National Toxicology Program includes a discussion of formaldehyde (gas). Although the report focuses on the carcinogenic nature of the gas itself, it includes the following description of formaldehyde that discusses formaldehyde in solution:

*Formaldehyde is a flammable, colorless gas with a pungent, suffocating odor. It is highly soluble in water (up to 55%), acetone, benzene, chloroform, diethyl ether, and ethanol. The gas is stable in the absence of water, but it is incompatible with oxidizers, alkalis, acids, phenols, and urea. Explosive reactions occur with peroxide, nitrogen oxide, and performic acid. Anhydrous gaseous formaldehyde is not available commercially. Most formaldehyde is sold as aqueous solutions, known as formalin, containing 30% to 50% formaldehyde with 0.5% to 15% methanol as a polymerization inhibitor.*²⁵ [emphasis added]

One of the areas of research chemistry where analysis of methanediol or methylene glycol shows promise is apparently the study of interstellar materials. But even in such discussions, which clearly acknowledge the distinction between methylene glycol (methanediol) and gaseous formaldehyde, there are descriptions of formaldehyde in solution at levels that the company’s position would render impossible. In reporting on the decomposition of “gas phase” methanediol to formaldehyde, for example, an article in the September 2003 *Journal of Chemical Physics* nonetheless refers to a “5% by weight aqueous solution of formaldehyde.”²⁶ The article also includes the useful explanation that, at “low” temperatures (below minus 280 degrees Fahrenheit), methanediol is essentially stable, while at “high” temperatures (above 80 degrees Fahrenheit) it “decomposes into formaldehyde and water.”²⁷ A temperature of 80 degrees may be described as a high temperature in the context of outer space, but it is certainly well within reach in the workplace (and off-gassing of formaldehyde begins at much lower temperatures). And the 80 degree threshold is considerably cooler than the temperature to which the solutions in question will be heated as part of the hair smoothing process.

²³See, for example, <http://www.cdc.gov/niosh/docs/2003-154/pdfs/2016.pdf> for a description of the HPLC/UV Method 2016) and <http://www.cdc.gov/niosh/docs/2003-154/pdfs/2541.pdf> for a description of the GC Method 2541). Further discussion of the methods can be found in the section entitled “Analytical Methods.”

²⁴ LA Testing, the laboratory relied upon by Health Science Associates to analyze the air monitoring samples referenced in the Brazilian Blowout’s October 15, 2010 statement, publicly advertises that it does bulk formaldehyde analysis using HPLC/UV.

²⁵*Report on Carcinogens*, 11th Edition, published by the National Toxicology Program of the Public Health Services Program of the United States Department of Health and Human Services. The report can be found at <http://ntp.niehs.nih.gov/ntp/roc/eleventh/profiles/s089form.pdf>.

²⁶David R. Kent IV, Susanna L. Widicus, Geoffrey A. Blake, William A. Goddard III, “A Theoretical Study of the Conversion of Gas Phase Methanediol to Formaldehyde,” *Journal of Chemical Physics*, Volume 119, Number 10 (September 8, 2003), p. 5119.

²⁷*Ibid.*, p. 5118. The original article gives the measurements using the Kelvin temperature scale, with the low temperature described as being less than 100 K and the high temperature described as being greater than 300 K. The Fahrenheit conversion in the text of the present discussion is used to provide a clearer context for the reader.

A further example comes from an article specifically discussing the conversion of gaseous formaldehyde to methylene glycol when formaldehyde is found in solution. In the course of the discussion about the equilibrium between gaseous formaldehyde and methylene glycol, the article's authors refer to "hydrated formaldehyde" and to "aqueous formaldehyde" as terms to describe the material in solution.²⁸

Occupational Regulations and Guidance

The 1992 federal OSHA Formaldehyde Standard (CFR 1910.1048), which is enforced in Oregon by Oregon OSHA, includes a number of provisions. In several sections, it makes it clear that the standard applies not only to gaseous formaldehyde, but also to formaldehyde in solution.²⁹ The standard's Appendix A, in discussing formalin, specifically references the term "methylene glycol."³⁰ The standard itself, federal OSHA technical bulletins, federal OSHA interpretive guidance,³¹ and federal OSHA discussions of analytical methods all make it clear that

²⁸J.G.M. Winkelman, O.K. Voorwinde, M. Ottens, A.A.C.M Beenackers, L.P.B.M. Janssen, "Kinetics and Chemical Equilibrium of the Hydration of Formaldehyde," *Chemical Engineering Science* 57 (2002) pp. 4067-4076.

²⁹See, for example, the following language from the federal standard (references to formaldehyde in solution have been highlighted):

- *Scope and application. This standard applies to all occupational exposures to formaldehyde, i.e. from formaldehyde gas, **its solutions**, and materials that release formaldehyde.* (CFR 1910.1048(a))
- *All contact of the eyes and skin with **liquids containing 1 percent or more formaldehyde** shall be prevented by the use of chemical protective clothing made of material impervious to formaldehyde and the use of other personal protective equipment, such as goggles and face shields, as appropriate to the operation.* (CFR 1910.1048(h)(1)(i))
- *If employees' skin may become splashed with **solutions containing 1 percent or greater formaldehyde**, for example, because of equipment failure or improper work practices, the employer shall provide conveniently located quick drench showers and assure that affected employees use these facilities immediately.* (CFR 1910.1048(i)(2))
- *If there is any possibility that an employee's eyes may be splashed with **solutions containing 0.1 percent or greater formaldehyde**, the employer shall provide acceptable eyewash facilities within the immediate work area for emergency use.* (CFR 1910.1048(i)(3))
- *Housekeeping. For operations involving **formaldehyde liquids** or gas, the employer shall conduct a program to detect leaks and spills, including regular visual inspections.* (CFR 1910.1048(j))
- *The following shall be subject to the hazard communication requirements of this paragraph: formaldehyde gas, **all mixtures or solutions composed of greater than 0.1 percent formaldehyde**, and materials capable of releasing formaldehyde into the air, under reasonably foreseeable conditions of use, at concentrations reaching or exceeding 0.1 ppm.* (CFR 1910.1048(m)(1)(i))

³⁰CFR 1910.1048 Appendix A, "Substance Technical Guidelines for Formalin."

³¹See, for example, the following interpretative statements from federal OSHA (references to formaldehyde in solution have been highlighted):

- ***Liquid formaldehyde** can also cause severe damage to the eyes. Thus, the standard requires employers to provide appropriate eye wash facilities within the immediate work area for emergency use by any employee whose eyes are splashed with **solutions containing 0.1 percent or more of formaldehyde**.* (December 12, 1989 response to questions about the standard).
- *In addition to the inhalation hazard, **solutions of formaldehyde (such as the formalin used as a tissue preservative)** can damage skin and eye tissue immediately upon contact. For this reason the standard requires effective protective equipment to prevent skin and eye contact, as well as eyewashes and showers if there is the possibility of splashes to eyes and body.* (May 16, 1990 response to questions about the standard's application in medical schools).
- *The severity of reactions to eye contact with **formaldehyde solutions** depends on the concentration of **formaldehyde in solution** and the amount of time lapsed before emergency and medical intervention. Accidental splashing of human eyes with **aqueous solutions of 37 percent formaldehyde (formalin)** has*

measurements of the formaldehyde content of materials in relation to the standard appropriately include aqueous formaldehyde. The two-page employer “fact sheet” designed as a quick reference to the standard’s requirements includes several references to formaldehyde in solution, beginning with the following statement:

Although the term formaldehyde describes various mixtures of formaldehyde, water and alcohol, the term “formalin” more precisely describes aqueous solutions, particularly those containing 37 to 50 percent formaldehyde and 6 to 15 percent alcohol stabilizer.³²

Federal OSHA is not alone in referring to formaldehyde in solution. As noted previously, NIOSH considers formalin to be “formaldehyde in solution,” as do a wide array of chemical, medical and toxicology guides and dictionaries. The Hazard Evaluation System & Information Service of the State of California’s Department of Health Services (in cooperation with the state’s Department of Industrial Relations) has published a fact sheet on formaldehyde that not only refers to formalin but also lists “methylene glycol” as one of several synonyms and trade names of formaldehyde products.³³

Regardless of the name used to refer to the solution, the hazards are the same. These solutions present a serious hazard to the eyes, skin, nose and lungs. OSHA regulations require the manufacturer to prepare a material safety data sheet for materials such as this and distribute to the end user so they are aware of the hazards.

Oregon OSHA and CROET continue to believe it is appropriate from a scientific, toxicological and regulatory standpoint to refer to liquid solutions as “containing formaldehyde” even though much of that formaldehyde has been at least temporarily converted to methylene glycol. At the same time, it should be noted if one were to substitute “methylene glycol” for all references to “formaldehyde in solution,” “aqueous formaldehyde,” or “hydrated formaldehyde” in laboratory reports and in lists of ingredients, such a substitution also would be necessary when discussing the hazards of “formaldehyde in solution.”

When one considers the well-known dangers of consuming the substance, of letting it come into contact with the skin, and of the likely production of gaseous formaldehyde, it is clear that “methylene glycol” must appropriately be considered a hazardous substance. In that light, there can be no question that a material safety data sheet that fails to acknowledge the hazards of formaldehyde using *either* the term formaldehyde or the term methylene glycol is inaccurate and violates the applicable rules when that product contains more than 0.1 percent formaldehyde using standard laboratory analyses. A hyper-technical argument over appropriate chemical nomenclature does not alter the applicable workplace health and safety requirements, nor should it be allowed to disguise the risks, even if inadvertently.

*produced a wide range of ocular injuries including corneal opacities and blindness. ...Skin contact with **formaldehyde solutions** can cause irritation of the skin and allergic contact dermatitis. These skin diseases and disorders can occur at levels well below those encountered by many formaldehyde workers. Symptoms include erythema, edema, and vesiculation or hives. Exposure to **liquid formalin** or formaldehyde vapor can provoke skin reactions in sensitized individuals even when airborne concentrations of formaldehyde are well below 1 ppm. (March 25, 1998 response to questions about the standard’s application to embalming in funeral homes).*

³²Found at http://63.234.227.130/OshDoc/data_General_Facts/formaldehyde-factsheet.pdf, p. 1.

³³Found at <http://www.cdph.ca.gov/programs/hesis/Documents/formaldehyde.pdf>, p. 1.

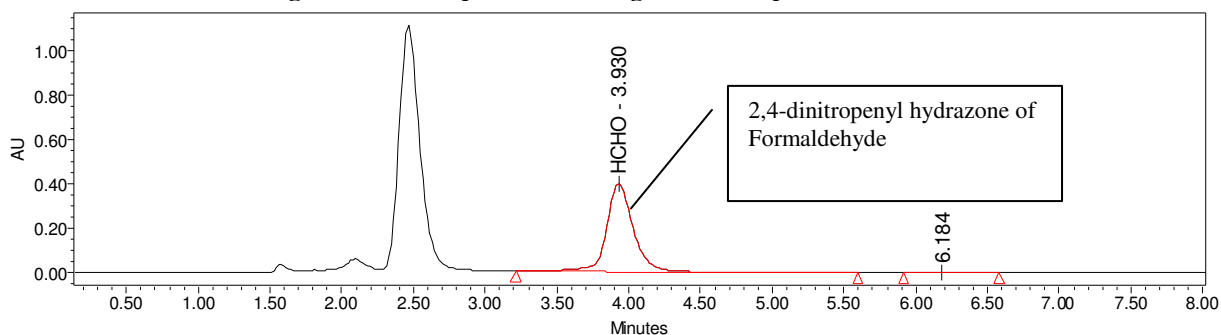
Analytical Methods

In analyzing the various hair smoothing samples, the Oregon OSHA Laboratory had the option of using several different analytical methods, both individually and as confirmation of one another. The methods chosen depended upon several factors, as described below.

Bulk Sample Analysis

Two Brazilian Blowout samples were initially analyzed using an analytical technique that can detect several aldehydes including formaldehyde, acetaldehyde and glutaraldehyde. This method was selected because the actual contents of the bulk samples were not known. The method derivatizes any aldehydes present with 2,4-dinitrophenyl hydrazine to form a hydrazone.^{34,35,36} One drop of bulk was weighed and diluted to 10 milliliters in water. 200 microliters of this solution was added to 2 milliliters of a 2,4-dinitrophenyl hydrazine solution in acetonitrile. The resultant mixture was analyzed by reverse phase High Performance Liquid Chromatography (HPLC) using a methanol/water eluent with a C18 column and a diode array detector. Analysis of the first two samples detected formaldehyde – and no other aldehydes. A third sample was analyzed later and it contained only formaldehyde as well.

High Pressure Liquid Chromatogram of sample 10-C2731



Several other methods were used to confirm the presence of formaldehyde in the first few samples received in the lab. The first method was the iced sulfite method used by the wood products industry to measure formaldehyde in the presence of urea formaldehyde resins.^{37, 38} About 0.3 grams of the sample was added to a mixture of sodium sulfite, magnesium chloride and thymolphthalein on ice. If formaldehyde was present a reaction with sodium sulfite produced sodium hydroxide and the solution turned blue. The amount of sodium hydroxide present was determined by back titration with hydrochloric acid to a clear endpoint.

³⁴Kazuhiro Kuwata, et. al, "Determination of Aliphatic and Aromatic Aldehydes in Polluted Airs as 2,4-Dinitrophenyl hydrazones by High Pressure Liquid Chromatography" *Journal of Chromatographic Science*, May 1979, Vol 17, p 264.

³⁵RK Bealey, et. al. "Sampling of Formaldehyde in Air with Coated Solid Sorbent and Determination by High Performance Liquid Chromatography" *Anal. Chem.* 1980, 52, 1110-1114.

³⁶DHHS (NIOSH) Publication 94-113 (August, 1994), NIOSH Manual of Analytical Methods (NMAM), Fourth Edition, FORMALDEHYDE: METHOD 2016, Issue 2, dated 15 March 2003.

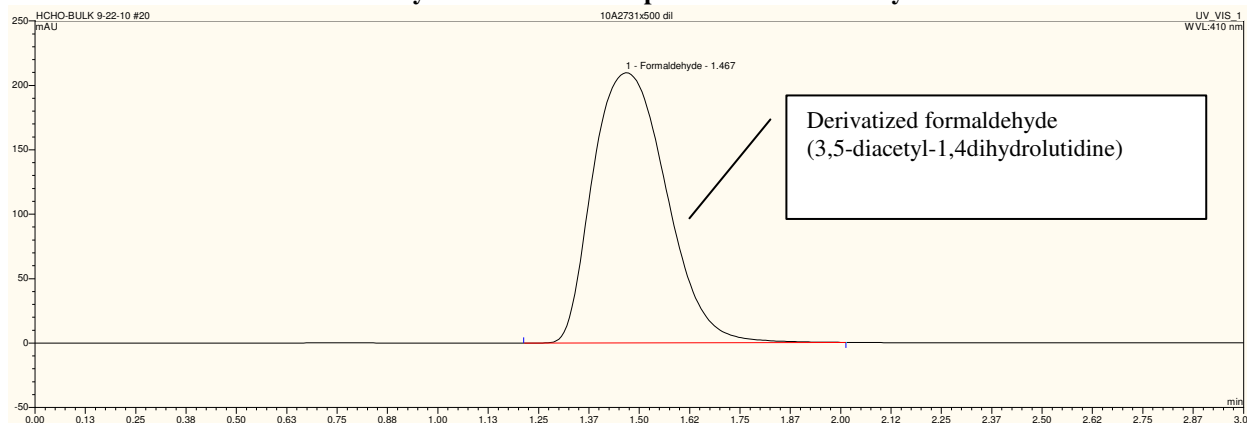
³⁷North American Test Methods (NATM) –E01.

³⁸OAR 437-002-1910.1048 appendix C 4.3.

The bulk samples were analyzed using a method based on derivatization of formaldehyde with 2,4-pentanedione (acetyl acetone).^{39, 40} A drop of the bulk was weighed and diluted to 10 milliliters with water. A solution of acetyl acetone in aqueous ammonium acetate was added to an aliquot of the sample. If formaldehyde was present the solution turned yellow. The concentration of formaldehyde was determined by ultraviolet–visible spectrophotometry at 412 nanometers.

The samples were also analyzed by HPLC using post column derivatization with acetyl acetone.^{41, 42, 43} This method is used in the European Union to determine formaldehyde in cosmetics. A sample was weighed and diluted to 10 milliliters in water. Depending on the final concentration the sample was diluted again 1 to 10 or 1 to 100. Analysis was performed on a reverse phase HPLC. The eluent was derivatized post column with acetyl acetone in aqueous ammonium acetate, and the presence of formaldehyde was detected at 410 nanometers. This method was used to analyze all of the samples received. It was selected because of its specificity for formaldehyde.

**High Performance Liquid Chromatogram of sample 10-C2731.
The formaldehyde was derivatized post column with acetyl acetone.**



Finally, a neat aliquot of three samples were injected onto a gas chromatograph-mass spectrometer. Large peaks with the retention time of formaldehyde were detected in each sample. These peaks were identified by mass spectral match.⁴⁴

³⁹ASTM International, ASTM Standards D-19 Proposal P 216, Proposed Test Method for Formaldehyde in Water, 1995.

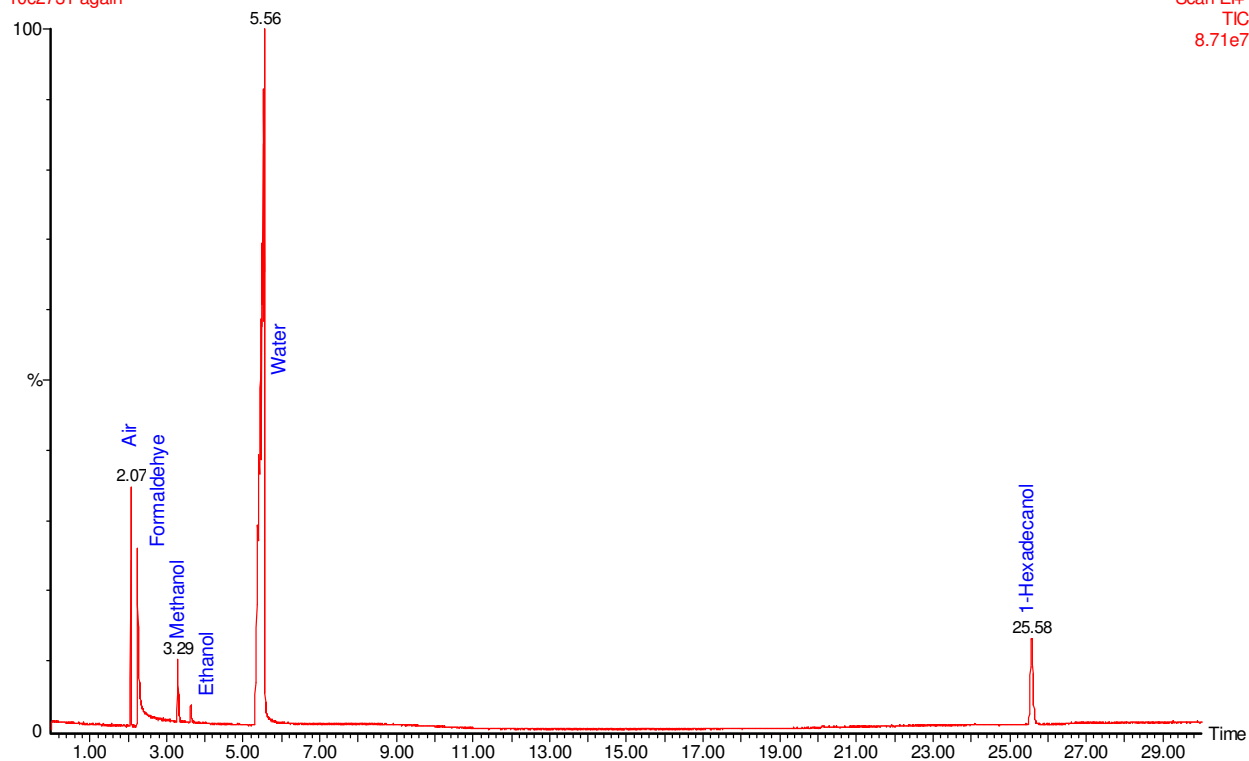
⁴⁰National Council for Air and Stream Improvement, Inc. (NCASI). 1990. Investigation of Methodology to Assess Gaseous and Releasable Formaldehyde from Paper and Wood Formaldehyde Resin Containing Dusts During the Use of Personal Samplers for Workplace Airborne Dust. Technical Bulletin No. 0597. Research Triangle Park, NC:

⁴¹European Union Official Journal of European Communities # L248 30/09/96 p. 001, IDENTIFICATION AND DETERMINATION OF FREE FORMALDEHYDE.

⁴²James Michels, “Improved measurement of formaldehyde in water soluble polymers by high performance liquid chromatography coupled with post column reaction detection”, *Journal of Chromatography A*, 914 (2001) 123-129.

⁴³ASTM International, ASTM D5910-05, Standard Test Method for Determination of Free Formaldehyde in Emulsion Polymers by Liquid Chromatography.

⁴⁴NIST/EPA/NIH Mass Spectral Library (NIST 02 from National Institute of Standards and Technology Standard Reference Program).



Air Sample Analysis

Analysis of all air samples taken was performed using NIOSH 2016.⁴⁵ Samples were collected on SKC 226-119 sorbent tubes at 0.05 to 0.2 liters per min. The 2,4-dinitrophenyl hydrazine on silica gel in the SKC 226-119 tubes reacts with any aldehydes present in the air. The contents of the tubes were placed in autosampler vials and desorbed in 2 milliliters acetonitrile. The tubes were analyzed by reverse phase High Performance Liquid Chromatography on a C18 column with a methanol/water eluent. Detection was at 353 nanometers with a diode array detector.

⁴⁵DHHS (NIOSH) Publication 94-113 (August, 1994), NIOSH Manual of Analytical Methods (NMAM), Fourth Edition, FORMALDEHYDE: METHOD 2016, Issue 2, dated 15 March 2003.

Summary and Discussion of Bulk Sample Results

Summary

A total of 105 samples of various hair-smoothing products were taken from 54 Oregon salons. Of these, 37 samples came from bottles of the Brazilian Blowout Acai Professional Smoothing Solution, labeled “formaldehyde free.” The formaldehyde content of these samples ranged from 6.8 percent to 11.8 percent and averaged 8.8 percent. An additional 19 of the samples were of Brazilian Blowout Solution (which is not labeled “formaldehyde free” but does not mention formaldehyde on its packaging or material safety data sheet). The formaldehyde content of these samples ranged from 6.4 to 10.8 percent and averaged 8.0 percent.

In addition to the Brazilian Blowout products, a limited number of samples also were taken of the following hair smoothing products:⁴⁶

- Brazilian Gloss Keratin Smoothing Gloss
- Keratin Express Brazilian Smoother
- Keratin Complex Smoothing Therapy
- Brazilian Keratin Treatment, Marcia Teixeira
- Chocolate, extreme de-frizzing treatment
- QOD Gold solution
- Kera Green Keratin
- Pravana Naturceuticals Keratin Fusion
- JKs Smoothing Treatment
- Bio Ionic Kera Smooth anti frizz

Although formaldehyde above the 0.1 percent threshold was found in all but the last three products listed, the results in all but the first case were between one eighth and one quarter of the results for Brazilian Blowout. The analysis of these products is summarized in the Table entitled “Summary of Results of Hair Smoothing Products.”

In addition, Oregon OSHA staff collected a limited number of samples of various “after care” products (because in at least some cases these products are promoted as having the same active ingredients as the hair smoothing treatments). A summary of these results is found in the table entitled “Summary of Other Hair Care Products,” while a more detailed list is found in the table entitled “Detailed Results of Other Hair Care Products.”

Generally, the formaldehyde content of such products was quite low (if not below detectable levels, at least below the 0.1 percent threshold). A few samples of the Brazilian Blowout shampoos tested just above the threshold (the majority tested well below the 0.1 percent threshold).

⁴⁶The samples collected were based on the products available in the salons visited, with particular emphasis on those hair smoothing products that advertised themselves as containing no formaldehyde or that did not indicate a formaldehyde risk on the material safety data sheet.

**Table 1: Summary of Results of Hair Smoothing Products
Oregon OSHA Analytical Laboratory**

Smoothing Treatment	Number of samples	Average Percent Formaldehyde	Highest Percent Formaldehyde	Lowest Percent Formaldehyde
Brazilian Blowout Solution	19	8.0	10.8	6.4
Brazilian Blowout Acai Professional Smoothing solution "Formaldehyde Free"	37	8.8	11.8	6.8
Brazilian Gloss Keratin Smoothing Gloss	1	7.3		
Keratin Express Brazilian Smoothing Treatment	7	1.2	1.2	1.0
Keratin Complex, Smoothing Therapy	3	1.9	2.3	1.7
Brazilian Keratin Treatment, Marcia Teixeira	4	1.6	2	1.2
Chocolate, extreme de-frizzing treatment	2	2.0	2.2	1.9
QOD GOLD SOLUTION	1	2		
Kera Green Keratin and Protein Hair treatment	2	1.5	1.6	1.4
JK's Smoothing Treatment	1	< LOQ ⁴⁷		
Bio Ionic Kera Smooth Anti Frizz	2	<0.01	0.01	<0.01
Pravana Naturceuticals Keratin Fusion	2	<0.01	<0.01	<0.01

**Table 2: Summary of Other Hair Products
Oregon OSHA Analytical Laboratory**

Product	Number of Samples	Average % Formaldehyde	Highest % Formaldehyde	Lowest % Formaldehyde
Coloring	2	<0.01		
Shampoo	9	0.05	0.15	<0.01
Conditioner	4	0.01	0.05	<0.01
Serum	3	0.05	0.06	0.05
Other	7	0.01	0.03	0.0005

Discussion of Oregon OSHA Bulk Sample Results

Apart from air monitoring or any other discussion of the hazards involved, several of the analytical results make it clear that the material safety data sheet (MSDS) must address the potential exposure to formaldehyde. Solutions with a measured formaldehyde content of more than 0.1 percent must list formaldehyde as an ingredient, describe the potential hazards, and discuss appropriate control measures to address those hazards.

The general requirements addressing communication about chemical hazards can be found in CFR 1910.1200. This "hazard communication" rule requires all manufacturers, importers, and distributors to provide an MSDS that lists all ingredients that are specifically regulated by OSHA, or have a threshold limit value (TLV) established by the American Conference of

⁴⁷"LOQ" stands for "limit of quantification" and indicates that the sample's formaldehyde content was below levels at which it could be quantified.

**Table 3: Detailed Results of Other Hair Care Products
Oregon OSHA Analytical Laboratory**

Product	Percent Formaldehyde
Brazilian Blowout Anti-Frizz Conditioner Maintaining Product	0.05
Brazilian Blowout Deep Conditioning Masque Maintaining Product	<0.01
Brazilian Blowout Acai Deep Conditioning Masque	<0.01
Brazilian Blowout Acai Deep Conditioning Masque	<0.01
Brazilian Blowout Acai Professional Anti-Residue Shampoo	0.05
Brazilian Blowout Shampoo	0.11
Brazilian Blowout Shampoo	0.04
Brazilian Blowout Acai Anti-Frizz Shampoo	0.01
Brazilian Blowout Anti-Frizz Shampoo	<0.01
Brazilian Blowout Anti Residue Shampoo	<0.01
Brazilian Blowout Acai Professional Anti-Residue Shampoo	<0.01
Brazilian Blowout Anti-Frizz Shampoo Maintaining Product.	0.11
Brazilian Blowout Anti Residue Shampoo	0.15
Brazilian Blowout Acai Daily Smoothing Serum	0.05
Brazilian Blowout Acai Daily Smoothing Serum	0.05
Brazilian Blowout Acai Daily Smoothing Serum	0.06
CHI Transformation System Bonder Phase 2 (Red)	<0.01
CHI Transformation System Bonder Phase 2	<0.01
CHI Transformation System Solution Phase 1 (Blue)	0.03
CHI Transformation System Solution Phase 1	0.03
CHI Transformation System Solution 1 Phase (Green)	0.03
Igora Royal Coloring System, used 1:1 ratio with colorant	<0.01
Igora Roral Color Creme	<0.01

Governmental Industrial Hygienists (ACGIH) or a recommended exposure limit (REL) established by the National Institute for Occupational Safety and Health (NIOSH). In addition, the MSDS must list any chemical for which there is statistically significant evidence based on at least one study that demonstrates that it can cause acute or chronic health effects in exposed employees.^{48,49} Such chemicals must be listed if they are found in the substance at a threshold of 1 percent for most chemicals, and 0.1 percent for known or suspected carcinogens.⁵⁰

In addition to the general Hazard Communication requirement, the Formaldehyde Standard (CFR 1910.1048) applies to formaldehyde as a gas, in a liquid solution, or any material capable of

⁴⁸CFR 1910.1200(d)(2).

⁴⁹It is this provision that makes it clear that, even if methylene glycol was a completely different substance than formaldehyde (it is not), manufacturers and distributors would still be required to address risks in relation to “methylene glycol” itself as part of the material safety data sheet. There are ample studies showing that aqueous formaldehyde results in acute and chronic health risks – and referring to the substance as methylene glycol does not affect the validity of those studies.

⁵⁰CFR 1910.1200(d)(5)(ii).

releasing formaldehyde.⁵¹ This standard also has specific provisions that trigger the hazard communications standard. The threshold quantity for formaldehyde is 0.1 percent. In addition to this requirement, the rule also requires that any material capable of releasing airborne formaldehyde in concentrations greater than 0.1 part per million (ppm) must be identified on the MSDS as formaldehyde.

Information that must be listed on the MSDS includes (but is not limited to):

- The permissible exposure limit (PEL) established by OSHA, the TLV, and any other recommended exposure limits identified by the manufacturer, importer, or distributor.
- All health effects, including acute, chronic, carcinogenicity, sensitization
- All precautions for safe handling and use, including protective equipment, engineering controls, and work practice controls.
- First aid and emergency procedures.

In addition to meeting these hazard communication requirements, the Formaldehyde Standard requires employers using materials above the 0.1 percent threshold to assess actual airborne exposures, as well as to meet other requirements related to personal protective equipment and emergency eyewash, depending upon the exact hazards involved.

⁵¹CFR 1910.1048(m)(1)(i).

Summary and Discussion of Oregon OSHA Air Monitoring Results

Summary

Air samples were taken in seven salons during treatment with Brazilian Blowout Acai Professional Smoothing Solution (labeled “Formaldehyde Free”). In each case the stylist treated only one client. Neither that stylist nor other stylists in the same salon treated any other clients on the day of sampling. The treatment is a three-step process in which the stylist combs in the solution, blow dries the hair and then heat treats it. The stylists were sampled during this process. Samples were also taken on adjacent people or in adjacent areas in six of the salons. The exposures varied widely depending on many factors, such as ventilation, room size, and duration of treatment. The highest exposure was 1.88 parts per million (ppm) for 26 minutes while blow drying the hair. The highest 8-hour time weighted average exposure was 0.331 ppm.

Like federal OSHA, Oregon OSHA has four airborne exposure levels for formaldehyde that are relevant to these exposures. The standard’s action level triggers additional requirements if the 8-hour time-weighted average (TWA) exceeds 0.50 ppm⁵² and the permissible exposure limit (PEL) prohibits employers from exceeding an 8-hour TWA of 0.75 ppm formaldehyde.⁵³ The highest exposure was 66 percent of the action level and 44 percent of the PEL. However, if the same stylist had performed one more comparable two-hour procedure in the course of the same day, the time-weighted-average would likely have been approximately twice as high, putting it well over the action level and at more than 85 percent of the PEL. A third comparable procedure would have been likely to result in exposures above the PEL.

In addition, and of particular concern in relation to this sample, the standard includes a Short Term Exposure Limit (STEL) of 2 ppm.⁵⁴ This exposure level cannot be exceeded for any 15 min period. As noted, the highest exposure documented (for a 26-minute period) was 1.88 ppm, which is 94 percent of the STEL. Given the presence of two fans during the procedure in question, it is not difficult to imagine a scenario where the STEL might be exceeded (at least by this stylist).

The Formaldehyde Standard includes additional requirements that are invoked when employees are exposed to airborne levels above an eight-hour average of 0.1 ppm, the employer must institute an annual training program – and must provide medical surveillance to employees reporting formaldehyde signs and symptoms.⁵⁵

When employees are exposed to levels exceeding the action level or the STEL, the employer also must perform periodic air monitoring and institute a medical surveillance program. When exposures exceed the PEL, the employer also must establish regulated areas and provide respiratory protection when other control measures, such as ventilation or work practices, cannot reduce the levels below the PEL.

⁵²1910.1048(b).

⁵³1910.1048(c)(1).

⁵⁴1910.1048(c)(2).

⁵⁵ 1910.1048(l)(1)(ii). This requirement is also independently triggered by the presence of materials containing more than 0.1 percent formaldehyde.

There are other organizations that have recommended exposure limits. Although they do not carry the force of law (as OSHA's limits do), they reflect the considered recommendation of the workplace health community.

The American Conference of Governmental Industrial Hygienists (ACGIH) established a threshold limit value ceiling level (TLV-Ceiling) of 0.3 parts per million (PPM) in 1992. This differs from an 8-hour limit because it limits exposures to 0.3 ppm at any time. In the 2001 "Documentation of Threshold Limit Values," this value was established to minimize irritation, primarily to the eyes and upper respiratory tract. ACGIH also recognizes formaldehyde as a suspected human carcinogen, based on animal studies that resulted in cancers in nasal cavities. In 2000, ACGIH added the "sensitizer," in recognition that the TLV may not protect sensitized individuals. The most recent ACGIH recommendation maintains the previously adopted language.⁵⁶ The ACGIH recommendation was exceeded in most of the air monitoring conducted by Oregon OSHA.

The National Institute for Occupational Safety and Health (NIOSH), which is part of the Centers for Disease Control and Prevention, has a recommended exposure level (REL) of 0.016 ppm as an 8-hour time weighted average, as well as a 15-minute short term exposure limit of 0.1 ppm.⁵⁷ NIOSH also considers formaldehyde to be a known carcinogen (which likely explains the particularly low recommended exposure levels). The NIOSH recommended limit were exceeded in all the air monitoring conducted by Oregon OSHA (the results reported by the company for stylists also exceeded the NIOSH limit, and the sample for the middle of the salon reached the NIOSH recommended limit for 8-hour exposures).

To provide some perspective, the exposure at 1.88 ppm formaldehyde ranks 6th among the 600 air monitoring samples for formaldehyde Oregon OSHA has collected during the past five years. It is just slightly higher than one particular sample taken during embalming, which measured 1.87 ppm.

Discussion of Air Sampling Scenarios

Case 1: The first salon was in Portland. It was a relatively small salon with roughly six stations. Each station had a chest high divider separating it from neighboring stations. The room had general dilution ventilation that was augmented with two fans. One blew across the client and the other blew toward the stylist. The stylist wore nitrile gloves. The stylist was sampled for airborne formaldehyde exposure during this process.

In this case the stylist took 34 minutes to apply the solution. The exposure was 1.26 ppm formaldehyde for this time period. The stylist took 26 minutes to blow dry the hair and 1.88 ppm formaldehyde was found for this time period. Two samples were taken during the heat treatment. The first sample was for 48 minutes. 1.35 ppm formaldehyde was found for this time period. The second sample was for 6 minutes and 0.369 ppm formaldehyde was found. The time weighed average (TWA) exposure for the 114 minutes to complete the treatment was 1.39 ppm. The 8 hour TWA, with no additional Brazilian Blowout treatments conducted in the salon, was 0.331 ppm. Two samples were taken in the reception area of the salon during this process.

⁵⁶2010 Threshold Limit Values and Biological Exposure Indices, ISBN 978-1-607260-19-6.

⁵⁷Found at <http://www.cdc.gov/niosh/npg/npgd0293.html>.

The first sample was for 91 minutes and 0.319 ppm formaldehyde was found. The second sample was for 26 minutes and 0.227 ppm formaldehyde was found.

The stylist's exposure was 44 percent of the eight-hour exposure limit (PEL) and 66 percent of the action level. In this case the stylist's highest short-term exposure was 94 percent of the mandatory short-term limit and more than 6 times the ceiling limit recommended by the ACGIH. One sample in the reception area exceeded the ACGIH recommended ceiling, as did the eight-hour average itself.

Case 2: The second salon was in a medium-sized room with about 8 stylists' stations downstairs. The building had an upstairs as well. There were no dividers between the stylist's stations and there was no general ventilation. A window and a door were left open during the procedure to increase ventilation. The stylist wore nitrile gloves.

This stylist took 13 minutes to apply the solution. The formaldehyde exposure during this time was 0.303 ppm. She took 20 minutes to dry the hair and the formaldehyde exposure was 1.45 ppm. The heat treatment took 12 minutes and the formaldehyde exposure was 0.273 ppm.

The stylist's average exposure during the treatment was 0.805 ppm and the 8 hour average was 0.075 ppm. An area sample was taken at an adjacent station and the formaldehyde was 0.2 ppm. In this case stylist's exposure was only 10 percent of the eight-hour exposure limit and 15 percent of the action level. Even with multiple treatments, she would have been unlikely to exceed either the PEL or the action level. However, the highest short-term exposure reached 73 percent of the mandatory short-term limit and was almost five times the ACGIH-recommended ceiling. The adjacent station reached 67 percent of the ACGIH-recommended ceiling.

Case 3: The third salon was in a very large room with a high ceiling and general dilution ventilation. A window was left open to increase ventilation. The client had shoulder length hair. The stylist wore nitrile gloves.

The stylist took 23 minutes to apply the solution. The formaldehyde exposure was 0.206 ppm. She took 13 minutes to blow dry the hair and the exposure was 0.472 ppm. She took 25 minutes to heat treat the hair. The formaldehyde exposure was 0.181 ppm. She did a second blow dry for 15 minutes and the exposure was 0.084 ppm. A 188-minute sample was taken upstairs. It had a concentration of 0.048 ppm formaldehyde. A sample taken for 24 minutes after the treatment was 0.045 ppm formaldehyde. A 15-minute sample taken after that had formaldehyde less than the limit of quantification.

The stylist's average exposure during the treatment was 0.219 and the 8 hour average was 0.035 ppm, 7 percent of the action level and less than 5 percent of the 8-hour permissible exposure limit. Even with multiple treatments, she would have been unlikely to exceed the PEL or the action level. Her highest short-term exposure was 24 percent of the mandatory short-term exposure level and 50 percent higher than the ACGIH-recommended ceiling.

Case 4: A fourth salon had 8 stylists in a large room with some partitions between stations. There were several adjacent rooms and the front and back doors were left open for ventilation. The stylist wore latex gloves (latex gloves are not recommended for use with formaldehyde). The client had shoulder-length hair.

The samples in this case were not identified by task. The first sample took 19 minutes and the formaldehyde exposure was 0.442 ppm. The second sample was for 47 minutes and the exposure was 0.34 ppm. The stylist's average exposure during the procedure was 0.369 ppm and her eight-hour average was 0.051 ppm. Two samples were taken on an adjacent stylist. Her first sample was for 16 minutes and formaldehyde was less than the limit of quantification. The second sample was for 57 minutes and the exposure was 0.121 ppm. A person away from the treatment process was also sampled. Her exposures were 0.045 ppm formaldehyde for the first 41 minutes and 0.112 ppm for the next 57 minutes.

Once again, the stylist's exposures were 10 percent of the action level and less than seven percent of the 8-hour limit, making it unlikely that even multiple treatments would result in exposures above either the action level or the PEL. The stylist's highest short-term exposure was 22 percent of mandatory short-term limit 50 percent greater than the ACGIH-recommended ceiling.

Case 5: The fifth salon was in an unusually large room with ceilings higher than 20 feet. The room had general ventilation. The stylist wore nitrile gloves.

The samples were not separated by task. The first sample took 17 minutes and the formaldehyde exposure was 0.108 ppm. The second sample was for 15 minutes and the exposure was 0.074 ppm. The stylist's average exposure during the treatment was 0.092 ppm and the 8 hour average was 0.006 ppm. This stylist was well under the action level, as well as the mandatory eight-hour and short term limits. In contrast to the other procedures sampled, her exposure was also below the ACGIH-recommended level, coming in at 36 percent of the recommended ceiling.

Case 6: The sixth salon was in a room with two large ceiling fans on ceiling of different heights. There were six stations and the stylist sampled was in the area with the highest ceilings. The doors were left open during the treatment process. The stylist had a fan that blew across the client and wore nitrile gloves.

Breathing zone samples were placed on the stylist during the process. The samples were changed every 15 minutes. Samples were also placed on a chair between stylist stations, behind the stylist, in the reception area, and near the trash receptacle. The highest 15-minute exposure for the stylist was 0.176 ppm while blow drying and ironing the hair. Her average exposure during the procedure was 0.059 ppm and the 8-hour average was 0.006 ppm. The area sample on the chair had a peak exposure of 0.295 ppm, an average during the 45-minute treatment period of 0.144 ppm, and an 8 hour average of 0.014 ppm. The area behind the stylist had a peak exposure of 0.206 ppm with an average during the treatment of 0.116 ppm and an 8 hour average of 0.011 ppm. All the samples in the reception area were less than the limit of quantification of 0.2 ug per sample. The area at the trash receptacle had a peak exposure of 0.227 ppm with an average during the treatment of 0.125 ppm and an 8 hour average of 0.012 ppm.

The stylist's exposure was well below the Oregon OSHA PEL of 0.75 ppm and about 9 percent of the short-term limit, making it unlikely that either limit would be exceeded even if multiple treatments had been conducted during a single day. It was about 60 percent of the ACGIH-recommended level. The areas around the stylist had higher concentrations of formaldehyde during the course of the treatment than those to which the stylist was exposed.

Case 7: The seventh salon had four stations with a false ceiling. No doors or window were left open and the stylist did not use any fans during the treatment. She did not wear gloves. Breathing zone samples were placed on the stylist during the process, which took 94 minutes. The samples were changed every 15 minutes. Samples were also placed to the right of the stylist, near the stylist's sink and to the left of the stylist. The stylist's peak exposure was 0.471 ppm, while applying the solution. Her average exposure during the procedure was 0.255 ppm and the 8 hour average was 0.050 ppm. The results did not exceed the 8-hour limit and it is unlikely that multiple treatments would have done so. The stylist's highest short-term exposure was about 24 percent of the mandatory short-term limit, although both her highest and second highest 15-minute exposures exceeded the ACGIH recommended ceiling of 0.3 ppm..

The area to the right of the stylist had a peak concentration of 0.157 ppm, with an average of 0.066 ppm and a 8-hour average of 0.013 ppm. The area near the sink had a peak concentration of 0.183 ppm. The area to the left of the stylist had a peak concentration of 0.160 ppm, an average of 0.062 ppm and an 8 hour average of 0.12 ppm.

Discussion of Oregon OSHA Results Compared to Brazilian Blowout's Reported Results

The company released air monitoring results on October 15, 2010, taken from two stylists performing two treatments each in a single salon. The only results reported were for the eight-hour average exposure, which came to 0.064 ppm for one stylist and 0.073 ppm for the other. The middle of the salon also was tested, providing an eight-hour average of 0.016.⁵⁸

In general, these results – although less detailed – are not inconsistent with Oregon OSHA's air monitoring results, which included both results that were higher and results that were lower than those reported by the company.

This exposure level is below both the action limit and the permissible exposure level.⁵⁹ Given Oregon OSHA's own results, however, both CROET and Oregon OSHA would be interested in the short-term exposure levels included in the company's sampling. It seems likely that the product used was relatively small and that ventilation, in keeping with the company's recommendations, was good. Assuming that the procedures took no more than two hours each (likely to be an overestimate), the average exposure during the procedure would be roughly half that reported for the eight-hour average.

If the procedures averaged no more than 75 minutes each (not an unreasonable assumption, given the time frames reported during the Oregon OSHA sampling), then the two stylists probably averaged more than 0.2 ppm during the procedure itself.

⁵⁸ Found at <http://www.brazilianblowout.com/pdf/october15.pdf>.

⁵⁹ As the standard notes, formaldehyde can cause signs and symptoms at much lower levels than the specified exposure limits, which is why the standard triggers a number of requirements at an 8-hour time-weighted average of 0.1 ppm. The action level and permissible exposure limits (PELs) can perhaps better be described as "danger" levels – they are regulatory levels of significance, and exceeding the PEL is a serious violation of the standard. While staying below the action level may mean that an employer is in compliance (assuming the air monitoring, medical surveillance, personal protective equipment, and hazard communication requirements of the standard also are met), it does not mean that formaldehyde levels are "safe."

Again, using Oregon OSHA's results for reference, it appears unlikely that the mandatory short-term levels were exceeded. However – given the level of variation observed during the Oregon OSHA air monitoring – it is quite possible that a 0.2 ppm average exposure over the course of a 75-minute treatment also would involve a short-term exposure in excess of the ACGIH-recommended ceiling of 0.3 ppm.

Discussion of the Potential Use of Air Monitoring Results by Other Salons

The Formaldehyde Standard requires each employer who is using formaldehyde or formaldehyde-containing products to “monitor employees to determine their exposure to formaldehyde.”⁶⁰ However, it provides for an exception for those employers who document “using objective data, that the presence of formaldehyde or formaldehyde-releasing products in the workplace cannot result in airborne concentrations of formaldehyde” above the action level or the short-term exposure limit “under foreseeable conditions of use.”⁶¹

In applying this exception, it is important to recognize its limited nature. For example, one set of results provided by the manufacturer – even if they show no possibility for exposures above the action level and the short-term exposure limit – would not allow all employers using a particular formaldehyde-containing product to disregard the requirement to engage in testing. The variations in Oregon OSHA’s own testing simply confirm the need for employers using these products to comply with the standard by obtaining air monitoring in relation to their own needs and situations. Even within a workplace, the employer must take into account variation between employees, looking either at “worst case” scenarios or at a random selection if worst-case scenarios cannot be identified.

The standard includes employee-specific air monitoring requirements precisely because such variations are the norm, rather than the exception. For hair stylists applying hair smoothing products that contain or can release formaldehyde, variables include the amount of product used, the length of time for each task, multiple applications of the product, the configuration of the station used by the stylist, the room volume of the salon, the type of ventilation, if any, and how the air in the salon moves. Variations also may result by particular application methods used by a particular stylist. One or two sample results below an established limit do not automatically guarantee that the product cannot result in exposures above those limits. They demonstrate only the exposure levels to those hair stylists at the time the air monitoring occurred.

CROET and Oregon OSHA note that ventilation is an important workplace control when respiratory hazards are confronted.⁶² But in assessing the potential risks of a product, it is the worst-case scenario that must be evaluated. If a manufacturer wishes to provide meaningful assistance to employers using its product, it will need to consider likely misuse or the potential to fail to follow instructions. In the case of a hair smoothing product, that means that the manufacturer would need to evaluate the product with little or no ventilation. It also means the manufacturer would need to consider the potential for overuse of the product and evaluate what effect that would have on exposure. It may be tempting to discard the highest Oregon OSHA results as atypical. They may indeed be atypical, but they are not unrealistic. And no employer using a similar product can assume that its results would be different without assessing the risk based on actual exposures in its own worst-case scenarios.

⁶⁰CFR 1910.1048(d)(1)(i).

⁶¹CFR 1910.1048(d)(1)(ii).

⁶²In discussing the importance of ventilation and the likelihood that stylists will adhere to their training regarding proper ventilation, it is worth noting the absence in the material safety data sheet of any reference to ventilation or to airborne hazards. When combined with the absence of any warnings regarding formaldehyde and the positive statement that no hazardous chemicals are present (and in some cases a label stating the product is formaldehyde free), as well as the emphasis on the use of “natural” ingredients and the absence of any “harsh chemicals,” one would expect to find at least some stylists using the product in the absence of the necessary ventilation.

Conclusion

Oregon OSHA and CROET have concluded that there are meaningful risks to salon workers when they are confronted with these hair smoothing products. Effective control of those risks depends upon accurate information regarding the potential hazards and the control measures available, which in turn begins with an accurate understanding of the ingredients and the potential harm they may cause.

In conjunction with this report, Oregon OSHA is advising Oregon salons and stylists that hair-smoothing treatments – particularly those generally referred to as “Keratin-based treatments”⁶³ – should generally be treated as formaldehyde-containing products and the requirements of the OSHA Formaldehyde Standard must be followed when there are employees under the Oregon Safe Employment Act (OSEA). Further, employers should be advised that any product that contains “methylene glycol” will continue to be treated as a formaldehyde-containing product under the OSEA.

⁶³It is worth noting that, although these products are often referred to using phrases such as “Keratin-based hair smoothing treatments,” CROET and Oregon OSHA have no concerns about keratin itself. Keratin is a naturally-occurring protein, and its presence in a product does not represent a known risk. Human hair is naturally made up largely of keratin.