Q&A: Understanding VOCs for Water-Repellent Materials for Concrete

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It has been said that water is the number one natural enemy to any structure, particularly for structures made from concrete, natural stone, or masonry. In Northern climates, water can penetrate structures and cause damage when it freezes, exerting tremendous pressure, and actually breaking concrete, stone, and masonry. Where deicing salts are used, or in seaside areas, water can carry salts to the interior of reinforced concrete, and these salts can cause or accelerate corrosion of steel reinforcing bar (rebar). As rebar corrodes, it also expands, which can result in cracks or breakage as well. On brick and concrete block, it is fairly common to see white, crusty deposits, known as efflorescence, on the surface. Efflorescence is a direct result of water penetrating and then evaporating from the surface. Efflorescence is unsightly and can damage some materials over time.

Water repellents help protect bridges and highways from water penetration and rebar corrosion. Courtesy of Dow Corning Corporation

Penetrating water repellents have been a mainstay of the protective coating and sealing markets for many years because of their ability to protect the aesthetic properties of structures and to provide protection against the damaging effects of water.

Silicon-based water repellents have been some of the most effective products of this type because of the unique benefits they offer with regard to penetration, durability, and aesthetic—they do not, as a general rule, substantially change a substrate's appearance. Over the past several years, water repellents, like most coatings, paints, and maintenance products, have been formulated to comply with tightening VOC regulations. As with paints, the challenge is to make water repellents that retain their performance properties while complying with the regulations. This article gives an overview to VOC content for water repellents.

Q. What, exactly, does VOC mean?

A. "VOC" is an acronym for "Volatile Organic Compound." Broadly defined, a VOC is any volatile compound of carbon that participates in atmospheric photochemical reactions. In water repellents and related materials, a VOC is typically a formulation ingredient that will evaporate (volatilize) under normal use. Probably the simplest example of a VOC would be a solvent or drying aid. Common examples include alcohols (like IPA), mineral spirits, kerosene, toluene, or xylene.

Sometimes the term VOC is used as a shorthand expression for Volatile Organic (Compound) *Content*. In either case, it is used to refer to the amount of VOC present in mass/volume. This amount is usually expressed as grams per liter (g/L) or, as common in paints, pounds per gallon (lb/gal).

Q. What geographical and application areas have implemented the most stringent VOC requirements in the U.S.?

A. On July 1, 2006, the South Coast Air Quality Management District (SCAQMD) in California implemented its architectural coating Rule 1113 , which has the most stringent VOC requirements in the U.S. SCAQMD is the air pollution control agency for all of Orange County and the urban portions of Los Angeles, Riverside, and San Bernardino counties.

At the state level, the California Air Resources Board (CARB) "oversees and assists the local air quality districts which regulate most non-vehicular sources of air pollution"

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(http://www.arb.ca.gov/html/brochure/arb.htm). As such, CARB does not regulate coatings, but through research, public comment, and industry input, does develop guidance documents called Suggested Control Measures (SCM) to assist districts in developing their architectural coatings rules. CARB SCMs are considered as "model rules," and their influence extends beyond California. The Ozone Transport Commission (OTC), a multi-state organization in the Northeast U.S., has repeated references to CARB in its own model rules and control measures. The OTC's use of CARB SCMs is expected to result in the adoption of similar rules and limits by agencies that regulate air quality in the Northeast, and quite probably other regions through future revisions. In other words, it is reasonable to expect that the rules we see in place in California today will influence a large portion of the U.S. in the next few years.

Because the SCAQMD has the most stringent current rules, the following district definitions of a few key coatings and penetrants may be of interest (Table 1).

Q. What are the VOC requirements for the applications listed above?

A. For SCAQMD, industrial maintenance coatings, primers, waterproofing sealers, and waterproofing concrete/masonry sealers manufactured after July 1, 2006, need to have a VOC content below 100 g/L. CARB is in the process of drafting revisions with similar limits for architectural coatings, and is hosting a series of workshops for review and discussion before finalizing their changes.

Q. How is the VOC content calculated to meet the SCAQMD regulations?

A. SCAQMD has its own method for determining the VOC content of coatings, SCAQMD Method 304. Method 304 and the more widely used EPA Method 24 are very similar, rely on the same principles, and use established ASTM methods for determining the VOC content of a coating. Most other air quality agencies use established EPA methods for determining volatile components and calculating VOC levels. These methods are detailed in "EPA Reference Method 24" (http://www.epa.gov/ttn/emc/promgate/m-24.pdf).

A variety of direct and indirect methods is employed to determine VOC content, but using the methods in Reference Method 24, the formula for calculating VOC in architectural coating is typically expressed as shown in the box on p. 18.

Q: Isn't there some question about the accuracy of the test methods used for determining volatile content?

A: There is general agreement that Method 24 has some level of inaccuracy for low VOC waterborne coatings. There is some debate about what methods can or should be used to determine the amount, and, more importantly, the type of volatile components. The methods currently approved cannot always adequately quantify or distinguish between different components, for instance, exempt, non-exempt, or water. The issues of inaccuracy with testing low VOC waterborne coatings have not been resolved, but SCAQMD, CARB, EPA, and ASTM, along with members of academia, are working to develop an improved test methodology to address the precision issues with Method 24.

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Table 1: Some Relevant Definitions of Coatings and Sealers from the SCAQMD

Architectural Coatings: Any coatings applied to stationary structures and their appurtenances, mobile homes, pavements, or curbs.
Industrial Maintenance Coatings: Coatings, including primers, sealers, undercoaters, intermediate coatings, and topcoats, formulated for or applied to substrates, including floors, that are exposed to one or more of the following extreme environmental conditions • immersion in water, wastewater, or chemical solutions (aqueous and non-aqueous solutions), or chronic exposure of interior surfaces to moisture condensation • acute or chronic exposure to corrosive, caustic, or acidic agents, or similar chemicals, chemical fumes, chemical mixtures, or solutions • repeated exposure to temperatures in excess of 250 degrees Fahrenheit • repeated heavy abrasion, including mechanical wear and repeated scrubbing with industrial solvents, cleaners, or scouring agents and • exterior exposure of metal structures
Primers: Coatings applied to a surface to provide a firm bond between the substrate and subsequent coats
Waterproofing Sealers: Coatings that are formulated for the primary purpose of preventing penetration of porous substrates by water
Waterproofing Concrete/Masonry Sealers: Clear or pigmented sealers that are formulated for sealing concrete and masonry to provide resistance against water, alkalis, acids, ultraviolet light, and staining

Data Source for the South Coast Rule 1113:
http://www.aqmd.gov/rules/reg/reg11/r1113.pdf

Q. Why are some organic compounds considered exempt from regulation?

A. Some compounds or solvents are specifically exempted because they have been shown to have negligible photochemical reactivity. This means these compounds do not react with sunlight to form ozone. Ozone is a chief component of smog and is considered an air pollutant and health hazard. Some examples of exempt compounds (at the federal EPA level) are volatile methyl siloxanes, acetone, and recently, tertiary butyl acetate. A complete listing is maintained in Federal Regulation 40 CFR 51.100(s). State or local agencies may not recognize the same exemptions, and in fact, there is only a partial exemption of t-butyl acetate (tBAc) in the SCAQMD for use in industrial maintenance coatings. CARB is currently amending the SCM for architectural coatings but is not proposing to exempt tBAc.

Q. How does dilution impact VOC content?

A. It really depends on how a product is diluted. If the product is diluted with a non-exempt solvent, the VOC content can be affected significantly, and usually increased. However, the situation is quite different and may be complex if water or exempt solvents are used alone or in conjunction with non-exempt solvents. If you are utilizing only exempt solvents, please see the next question.

Q. How do VOC-exempt solvents impact the amount of VOC?

A. If only exempt solvents or water is used for dilution, the VOC content changes very little. This is because these diluents are factored out or subtracted from the overall calculation, and the VOC content of the remaining ingredients is all that matters. Using exempt solvents may change the VOC content slightly because it may change the density of the final formulation.

Q: Aren't some of these rules and determinations a bit controversial?

A: VOC content calculation has long been a source of controversy. For instance, what really constitutes a volatile component? Vapor pressure, evaporation rate, temperature, time, and other chemical or physical properties all play a role. Some reaction by-products could evolve into volatile components after days, weeks, or longer.

Factoring out exempt compounds doesn't really acknowledge that total amounts of VOC can decrease. As an example, a product that is 95% water and 2.5% solvent (so 2.5% active) can theoretically have the same calculated VOC level as a product that is 50% solvent and 50% active. SCAQMD's Rule 1113 attempts to addresses this issue with its Low-Solids Coating category. For coatings that contain one pound or less of solids per gallon, as in this example, the coatings are regulated by the "VOC of material," which allows the calculation of VOC to be "inclusive," or to not factor out the exempt solvents or water.

However, the current EPA regulation only makes allowance for low solids classification for wood preservatives and stains (http://www.epa.gov/ttn/atw/183e/aim/fr1191.txt).

Therefore, the definition can vary by agency, and the issue still remains that a product that is predominantly water may calculate to a higher VOC level than one that contains a significant level of solvent.

Questions on these topics are a source of debate and eventual refinement of the definitions and standards. As a result, new standards and definitions are created, and the science gets better. Recently, there have been proposed changes in regulations because it is recognized that not all VOCs are equal in their contribution to ozone production. It is an evolutionary process, however, and so we have to work with what we have. As responsible companies, we continue to work with government and standards organizations to make regulations that are good for people, the environment, and business.

Q. Won't low VOC regulations make it impossible to make or sell some products? Or won't they be inferior?

A. Certainly, as the regulations tighten, they present more challenges. Using less solvent will probably make some types of coatings nearly obsolete, as has been the case for lacquer types of paints used in auto body finishing. Also, there are some applications where specifications may dictate using higher VOC products, and so specifications will clash with regulation. A good example of this for water repellents is that some departments of transportation specify a certain

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Calculating VOCs–EPA Method 24

Grams of VOC per liter of coating, less water and less exempt compounds, is the weight of VOC per combined volume of VOC and coating solids:

$$\text{VOC (grams/liter)} = \frac{Ws - Ww - Wes}{Vm - Vw - Ves}$$

Where:

Ws = weight of volatile compounds in grams
Ww = weight of water in grams
Wes = weight of exempt compounds in grams*
Vm = volume of material in liters
Vw = volume of water in liters
Ves = volume of exempt compounds in liters

*This calculation excludes or factors out water and other exempt compounds in calculating VOC content.

percentage of reactive silanes to effectively protect concrete structures, but there is no way to meet these specs and still have the required VOC due to the chemical realities of these materials. In this case, the specifications may need to evolve to be performance-based, not composition-based. The products will have to evolve as well, but that's the kind of challenge we chemists like to have, and I believe we can meet it.

There may be some trade-offs for performance versus regulation, but overall, coating and treatment manufacturers will be able to meet the challenges, make good products, and still help lower VOC emissions. In time, regulations may evolve, as well. Within the water repellent industry, it is widely held that there are higher-VOC products, such as alkoxy silanes, that, because of their penetration and durability, may last for 10 or more years. Consequently, these products could have less impact on air quality than lower VOC coatings that are not as durable or effective (based on testing) and may last for only a few years and so must be repeatedly reapplied. There has also been some activity around the regulations recognizing that not all VOCs are equal in their contribution to ozone production.

Q. How do I find the VOC requirements for coatings and water repellents outside of California?

A. Contact your state department of environmental quality to understand your local VOC requirements and calculations.

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Editor's Note: Readers wishing to compare their state and local VOC rules with the federal rule can find the latter in Title 40 of the Code of Federal Regulations, Part 59, sections 400–413, available through the U.S. government portal, www.gpoaccess.gov/.