

Emission Factors for Liquid Organic Peroxide Catalysts used in the Open Molding of Composites

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Introduction

Small quantities of highly reactive liquid organic peroxide solutions are used by the reinforced plastics industry to initiate the polymerization reaction (also referred to as "curing") in the resin or gelcoat material. These solutions are commonly called "catalysts," and are known by the commercial trade names Butanox™, Lupersol™, Thermacure™ or Hi-Point™. In order to start the curing reaction, enough catalyst solution is added to the resin or gelcoat material until about 1% to 2% of the material weight consists of catalyst. The catalyst solution is either sprayed together with the resin or gelcoat during spray lay-up (Mechanical), or a carefully measured amount of catalyst is stirred into a pail or bucket of resin for hand lay-up (Manual).

Most organic peroxide catalysts consist of a 30% to 47% solution of methyl ethyl ketone peroxide (MEKP) dissolved in dimethyl phthalate (DMP). The DMP acts as is a stabilizing agent to prevent the spontaneous detonation of the MEKP at room temperature. A trace amount of methyl ethyl ketone (MEK) may also be present as a contaminant byproduct left over from the manufacture of the MEKP.

MEKP

MEKP is a highly reactive, colorless liquid organic oxidizer, with a pungent burning odor, which has the following properties:

CAS registry number	1338-23-4
molecular formula	CH ₃ COCH ₂ CH ₃ O ₂
vapor pressure	less than 0.1 mm Hg at room temperature

Contrary to a popular misconception, MEKP does not decompose into MEK after being sprayed together with resin or gelcoat. Instead, the MEKP is immediately consumed by the resin to initiate the curing process, so no MEKP is released. If a trace amount of MEKP does not fully react with the resin or gelcoat, a small amount of acetic acid droplets may be formed due to reactions with moisture present in the air - but not MEK. Acetic acid droplets are neither a HAP nor a VOC. Therefore, the normal usage of MEKP at reinforced plastics facilities will not result in any measurable VOC or HAP emissions whatsoever.

DMP

DMP is a colorless, oily, viscous organic liquid with a faintly sweet, ester-like odor, which has the following properties:

CAS registry number	131-11-3
molecular formula	C ₁₀ H ₁₀ O ₄
vapor pressure	less than 0.01 mm Hg at room temperature

DMP is both a VOC and a listed HAP. Fortunately, DMP has an extremely low vapor pressure resulting in practically no evaporation at room temperature. DMP vapor emissions from catalyst solutions are probably extremely small, but are still non-zero. The following five-step theoretical approach is employed to determine a reasonable non-zero emission factor for DMP:

1. According to the UEF model, a 50% styrene-content resin applied by spray gun will emit about 18.1% of the available styrene monomer before the resin cures. After curing, these emissions from the resin essentially stop.
2. DMP emissions will also emit a trace amount of vapor before the resin cures, and will follow the same general evaporation mechanisms as for the styrene monomer.
3. The ratio of vapor pressures for DMP to styrene is 0.01 mmHg ÷ 4.5 mmHg = 0.0022.
4. The evaporation rate for typical VOC species is proportional to the VOC vapor pressure.
5. Hence, the emission factor for DMP will be $0.0022 \times 18.1\% = \mathbf{0.040\% \text{ of available DMP by weight.}}$

Note that DMP emissions will be practically negligible at nearly all reinforced plastics facilities in the USA. For example, a plant using one million pounds of resin (which is a relatively large amount) would only emit the following amount of DMP vapor:

$$1,000,000 \text{ lb/yr resin} \times 1.5\% \text{ catalyst} \times 60\% \text{ DMP} \times 0.04\% = \mathbf{3.6 \text{ lb/yr DMP emissions}}$$

This amount of DMP will be very small, so record-keeping and reporting requirements for DMP emissions from catalyst usage do not seem to be warranted.

MEK

MEK is another VOC and listed HAP, which may be a trace contaminant byproduct of the precursor chemical reactions employed to produce MEKP. However, the amount of contamination is reportedly very small - normally from about 50 ppm to a maximum of 1% by weight of MEK may be present in the raw MEKP feedstock used to make commercially-available catalyst formulations. Presumably, all of this trace amount of MEK will be released during the lamination process, because the MEK will neither react nor combine with the polyester resin during curing. However, as in the case of DMP emissions discussed above, these MEK emissions will be insignificant at nearly all reinforced plastics facilities in the USA. For example, a plant using one million pounds of resin would emit no more than the following amount of MEK vapor at a maximum contamination level of 1% MEK in the MEKP feedstock and assuming a 40% MEKP concentration in the catalyst:

$$1,000,000 \text{ lb/yr resin} \times 1.5\% \text{ catalyst} \times 1\% \text{ MEK} \times 40\% \text{ MEKP} = \mathbf{60 \text{ lb/yr MEK emissions}}$$

The actual emission of MEK would probably be lower, because most catalysts formulations use MEKP with much less than 1% MEK contamination. The actual MEK contamination in a specific catalyst formulation can be obtained from the catalyst supplier. The amount of MEK emissions will be so small that record-keeping and reporting requirements for MEK emissions from catalyst usage do not seem to be warranted.

The above information regarding MEKP, DMP, and MEK emissions may be confirmed by contacting Dr. Frank Long, a leading authority on organic peroxides, who works for the Norac Company, one of the two major manufacturers of catalyst materials for the reinforced plastics industry. Dr. Long may be reached at (626) 334-2908, or at info@norac.com. The information provided by Dr. Long can be verified by contacting Mr. Brice Milleville, another authority on MEKP catalysts, who works for Akzo Nobel, the second major manufacturer of MEKP catalysts.

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