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Influence of volatile organic compounds emissions from road marking paints on ground-level ozone formation: case study of Kraków, Poland

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Abstract

Ground-level ozone, worldwide recognised amongst key pollutants responsible for smog and a significant pulmonary irritant is formed in troposphere *via* a photolytic process from nitrogen oxides (NO_x). Volatile Organic Compounds (VOC) during their decomposition in the atmosphere interact with NO_x and thus affect ozone formation. Their interactions are not equal and have been quantified in Maximum Incremental Reactivities (MIR). Using MIR, calculated was ozone formation potential of VOCs emitted from an aromatic solvent-containing paint that is used for marking of roads in Kraków, Poland. To simulate possible environmental benefits of using alternative materials, analysis was then extended to model paint without aromatic solvent and a waterborne paint. Ozone formation potential of the road marking paint currently used as standard in Kraków was calculated to be more than twice the amount of VOCs it emits: 240 kg of solvents evaporating from one tonne of paint might cause formation of over 550 kg of ozone – in Kraków that means up to 42 tonnes of tropospheric ozone annually. Elimination of the aromatic solvent would not lead to lesser VOC emissions, but decrease ozone production capability by about 50%. Further reductions could be realised with waterborne paint – VOC emissions lowered by 79% and potentially formed ozone reduced by up to 93%.
A cradle-to-grave Life Cycle Assessment (LCA) performed on the three analysed paints demonstrated that durability is the main environmental impact factor. Assuming service life achieved at our test field, where modern waterborne paints applied at 600 µm wet film and reflectorised with properly selected high-performance glass beads complied with the specification for two years, they definitely are more sustainable choices as compared to solventborne materials.

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Quantification of the effect of produced ozone on health was beyond the scope of this work, but based on literature reports a measureable effect is anticipated due to a well-documented correlation between increased tropospheric ozone level and increased mortality and morbidity.

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Keywords: Road marking; waterborne paint; solventborne paint; glass beads; tropospheric ozone; VOC; Life Cycle Assessment; Kraków; road safety; MIR; environmental protection

1. Introduction

Since white line was first painted on a road in 1911 in Michigan, U. S. A., horizontal road markings became ubiquitous, essential safety feature of modern roads. It was observed that in the city of Kraków, Poland almost all road marking is done with thin-layer application of a solventborne toluene-containing paint. Toluene, an aromatic solvent, is generally recognised as harmful to people and environment; on the other hand, its relatively low price, convenient solubility parameters, and evaporation rate make it a preferred choice for solventborne road marking paints, unless banned by a legislation.

The topic of troposphere ozone formation caused by road marking paints have been introduced only very recently, with the first brief note done by Scorgie (2011) and recently by Burghardt (2016).

Knowing of extreme air pollution in Kraków, we postulated that an improvement could be achieved by limiting the VOCs emitted from road marking paints and consequently the formed tropospheric ozone. The currently used road marking system and readily-available alternative paints are analysed herein.

2. Background

2.1. Horizontal Road Marking Materials

Solventborne paints were historically the first road marking materials and still remain in use as they are rather inexpensive and easy to apply, albeit not very durable. Their base resins have changed over time from chlorinated rubber, through alkyds, to acrylics. Film formation is achieved by simple evaporation of organic solvents.

Thermoplastic materials, which are in use since the 1940s, are based on rosin or petroleum derivatives – they are easy to apply and quite durable at the high applied thicknesses. Because they are solvent-free, emissions at the time of application are considered negligible, so they shall not be discussed herein.

A plethora of plural-component materials, comprising epoxy- or urethane-based paints, rely on film forming by chemical reaction taking place on the road surface. Drawback of these highly durable systems that can be prepared in solventborne, water-reducible, or solvent-free versions is relative toxicity of raw materials. These paints are seldom used in Europe and are not specifically included in this analysis. For their solventborne versions, the same composition of emissions as for solventborne paints may be presumed.

Coldplastics are widely used modern materials – they are applied to road surface in the form of acrylic monomers, which polymerize *in situ* to form durable films of thicknesses ranging from 300 μm (coldspray plastic) to 4 mm (structured marking coldplastic). This solvent-free technology is not included in this work.

First waterborne paints were developed in the 1980s, but because they dried very sluggishly, particularly in unfavourable weather conditions, they were not a big commercial success; nevertheless, the early technology is still in use today as it furnishes quite durable, stable, and rather inexpensive paints that work excellent in hot and dry climates. A conceptual break-through occurred with the development of quick-set technology for waterborne binders, patented by Clinnin et al. (1991). The technology employs polymeric materials that can be kept intermixed and suspended in aqueous media only at high pH – upon drop of pH, irreversible chemical reaction and curing occurs. Numerous modifications to the binders resulted in significant increases in durability and stability, meaningful shortening of drying, and other desired properties. Waterborne paints are essentially devoid of toxic materials and their VOC emissions are marginal.