eVOC SERBIA

REDUCTION OF EMISSIONS OF VOLATILE ORGANIC COMPOUNDS DUE TO THE USE OF ORGANIC SOLVENTS IN CERTAIN ACTIVITIES AND INSTALLATIONS

REQUIREMENTS FOR PAINT MANUFACTURING INDUSTRY

Norway

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This brochure has been prepared within the project "Implementation of European Regulation on Volatile Organic Compounds Emissions (eVOC Serbia)" implemented by the Cleaner Production Centre of the Faculty of Technology and Metallurgy, University of Belgrade and financially supported by the Royal Norwegian Embassy in Belgrade.

The eVOC Serbia Project is being implemented with the aim of achieving environmental and VOC emission standards. The Project provides assistance to the Ministry of Environmental Protection of the Republic of Serbia and the Serbian Environmental Protection Agency in transposing the chapter of the Industrial Emission Directive pertaining to operators and activities that use organic solvents, and provides full support to operators in Serbia, primarily small and medium-sized enterprises, by strengthening their capacities.

The Project Info Centre is available for all questions regarding organic solvents management and VOC emissions for each stakeholder, which will ensure more effective implementation of the Serbian VOC Regulation, thus making a greater contribution to environmental protection. In addition, one of the goals of the Info Centre is to improve knowledge and awareness about VOCs and their use, as well as the impact of these compounds on human health and the environment.

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1 INTRODUCTION

Volatile organic compounds (VOCs) encompass a very wide range of organic compounds characterized by high vapour pressure at lower temperatures, which gives them significant volatility already at room temperatures. This group comprises over 10,000 currently known compounds, such as methane, benzene, xylene, propane and butane.

Although they can be naturally occurring as well, from the legislative viewpoint, the important VOCs are those arising from different anthropogenic activities. They have a wide industrial application, primarily as organic solvents, which means they can be found in many paints, coatings and adhesives – and consequently, in many objects and products we use every day. Typical activities where they are used include printing, paints and coatings manufacture, coating activities, production of construction materials, production of furniture and wood products, as well as dry cleaning.

The intensity of health and environmental effects of volatile organic compounds primarily depends on the type of compound, its concentration and exposure time. Long-term indoor exposure can cause fatigue, headache, nausea, eye, nose and throat irritation in sensitive persons, but also damage the central nervous system and other organs. Not all VOCs show harmful health effects, but some can have carcinogenic and mutagenic effects or affect reproduction (CMR substances).

Environmental impacts of volatile organic compounds are primarily seen in the decreased air quality, but they can also be found as water and soil pollutants. In the atmosphere, they lead to the formation of the harmful ozone and photochemical smog in the lower layers of the atmosphere, and contribute to formation of acid rain and greenhouse gases. In the presence of sunlight, VOCs produce ozone by reacting with nitrogen oxides and carbon monoxide. In the troposphere, ozone increases the formation of fine particles in the air, and the mixture of ozone, particles and other gaseous pollutants is known as smog. In addition to lowering visibility, substances in smog can affect the plant health, lowering yields of seeds and pollination efficiency, and they can have harmful effects on respiratory systems of humans and animals.

In the European Union, the key legislative instrument for the reduction of industrial emissions of VOCs is the Industrial Emissions Directive (IED) (2010/75/EU), or, more precisely, its Chapter V. This chapter lists the special requirements for industrial installations using volatile organic compounds in their production processes. Provisions of Chapter V of the Directive pertain to 20 types of activities which use organic solvents, and operators who manage installations where such activities take place are obliged to undertake all necessary measures to comply with them. Technical provisions pertaining to installations and activities using organic solvents are listed in Annex VII of the Directive.

In the Republic of Serbia, the key document in this field is the Regulation on the list of industrial installations and activities for which volatile organic compounds emissions are controlled, on the values of volatile organic compounds emissions at a certain solvent consumption and total emission limit values, as well as an emissions reduction scheme (“Official Gazette of the RS”, no. 100/11). Implementation of the Regulation began on 1 January 2013, and it prescribes the obligations of operators engaged in one or more of 20 activities relevant for volatile organic compounds emissions, which exceed the prescribed annual thresholds for solvent consumption. All key provisions regarding the list of activities, substitution of certain substances with less hazardous alternatives, selection of a reduction scheme, manner of elaborating an annual solvent mass balance, monitoring and reporting obligations, annual consumption threshold and annual emission limit values for flue gas and emission limit values for fugitives for each activity are all prescribed in the Regulation.

2 WHO IS CONCERNED?

The VOC regulation applies to twenty categories of industry activities using volatile organic solvents. If the total annual solvent consumption of an installation performing manufacture of coatings, varnishes, inks and adhesives is equal to or greater than 100 t/year, the installation is subject to the requirements of the VOC Regulation and classified as a VOC operator.

According to the current legislation, a volatile organic compound (VOC) is any organic compound, including a fraction of the creosote, which has, at the temperature of 293.15K a vapour pressure of 0.01 kPa or greater, or the equivalent volatility under the conditions of temperature and pressure under which it is used.

Manufacture of coatings, varnishes, inks and adhesives is defined as:

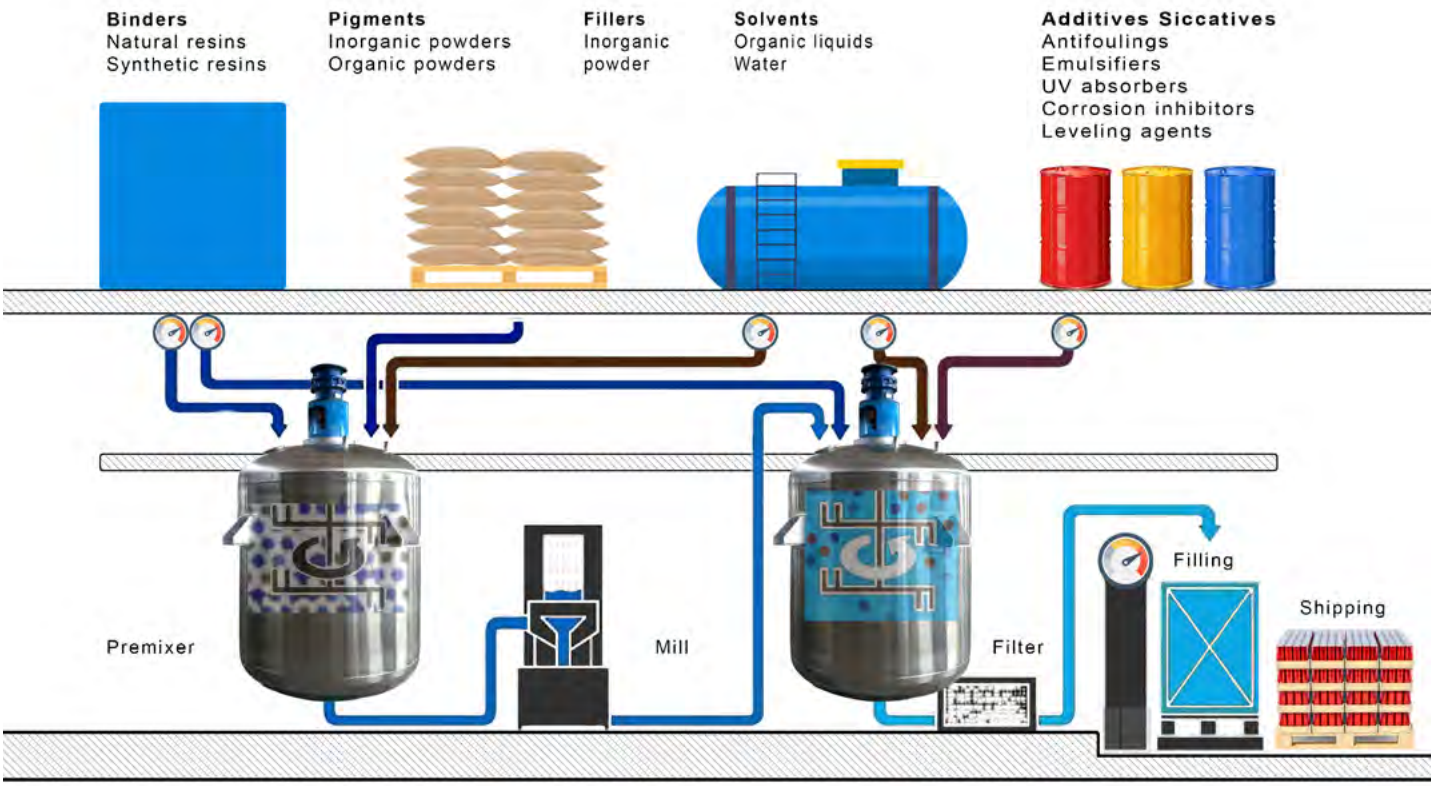
Production of final coating products, varnishes, paints and adhesives, as well as intermediates if they are produced in the same installation, by mixing pigment, resins and adhesive materials with organic solvents or other substances that act as vehicles, including in dispersive and pre-dispersive processes, thickness and colour adjustment, as well as filling the final products into containers.

2.1 Production process

The manufacturing process is generally a batch process, which involves combining raw materials, in one or more steps, to produce the finished product. All coating materials are comprised of appropriate mixtures of four main raw material component categories:

- resins (organic (usually) or inorganic polymers);
- pigments (primary (colours), extenders/fillers or actives (e.g. anti-corrosives);
- carriers (organic solvents, water, non-volatile liquids); and
- additives (a wide range of specific materials, used in small quantities to provide particular properties during manufacturing, in storage, during application, in service life etc.).

The main sources of VOC emissions in the installation are filling of vessels, dispersers and containers, leaking and spilling during material transfer, inappropriate handling (open vessels etc.) as well as cleaning of parts and the working environment. Other process steps with potentially important VOC emissions are storage tank breathing and loading, and emissions from solvents recovery.



Reference: Unsere Zukunft. Unser Lack – Eine Information der Österreichischen Lackindustrie im Fachverband der Chemischen Industrie; 2008 lackfibel.pdf (fcio.at)

3 WHAT ARE THE REQUIREMENTS FOR THE OPERATOR?

3.1 Registration

In line with the Regulation, operators in the Republic of Serbia, who perform one or more activities using organic solvents and exceed the solvent consumption threshold prescribed in Annex 2 of the Regulation (VOC operators) are obliged to:

Monitor and submit data to the Environmental Protection Agency, by filling in and submitting a form provided in Annex 3 of the Regulation. The form includes administrative and technical information on the company, activities performed, and quantities and types of used solvents.

3.2 Protection Against Harmful Volatile Organic Substances

The VOC Regulation provides special protection against harmful substances. Hazardous substances or mixtures that are classified as carcinogenic, mutagenic or toxic for reproduction (CMR) based on the volatile organic compounds they contain, i.e. those with hazard statements H340, H350, H350i, H360d or H360f shall be replaced, as far as possible, with less harmful substances or mixtures within shortest possible time. In addition, operators using compounds with the aforementioned hazard statements or risk phrases must comply, as soon as possible, with emission limit values for such compounds prescribed in Article 8 of the Regulation.

3.3 Compliance with emission limit values

In line with the Regulation, operators in the Republic of Serbia, who perform one or more activities using organic solvents and exceed the solvent consumption threshold prescribed in Annex 2 of the Regulation (VOC operators) are obliged to:

Ensure that volatile organic compound emissions from installations remain within the range of the allowed emission limit values for waste gas and for fugitive emissions, or within total emission limit values prescribed in the Regulation (Annex 5 of the VOC Regulation).

Based on the total annual solvent consumption, VOC operators are classified as small or medium installations. The emission limit values prescribed in Annex 5 of the VOC Regulation for these installations depend on this classification.

Annual solvent consumption, t/year	ELV for waste gas stack emission[i], mgC/Nm^3	ELV for fugitive emissions, % of solvent emission	Total emission, % of solvent input
100-1000	150	5	5
>1000	150	3	3
[i] VOC emission expressed as total organic carbon under normal conditions			

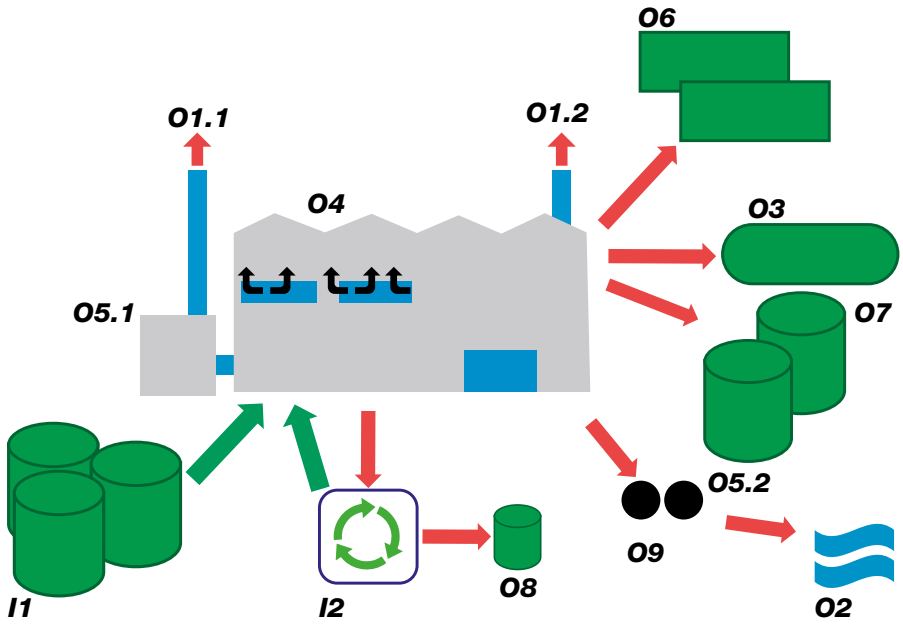
3.4 Demonstration of compliance

The installation operators have to demonstrate compliance with ELVs by elaborating an annual solvent mass balance for organic solvents in line with the procedure from Annex 4 of the Regulation. The purpose of elaborating this balance is to:

1. Determine the solvent consumption (SC), i.e. check whether Regulation applies to the installation (status of VOC operator);
2. Check compliance of VOC emissions from the installations against emission limit values prescribed in Annex 5 and Annex 6, or target emission values prescribed in Annex 7;
3. Identify opportunities for further decrease of solvent consumption.

The calculation includes the data on solvent consumption, its reuse, emissions of VOCs into air and water, as well as VOC emissions from waste and final products.

The annual solvent mass balance is elaborated every year for the previous year and kept for two years. VOC operators should regularly submit the data from their annual solvent mass balance to the Serbian Environmental Protection Agency. The form that the operators fill in and submit to the Agency, which is in the form of an Excel spreadsheet (VOC Regulation form) is available on the Agency's website:
http://www.sepa.gov.rs/index.php?menu=20168&id=18&akcija=showXlinked



The solvent mass balance follows the simple principle of a balance between inputs and outputs. It covers the total annual solvent input and output for an installation. However, not all of these quantities are relevant for the production of coatings, varnishes, inks, and adhesives.

$$\underbrace{I1 + I2}_{\text{TOTAL INPUT}} = \underbrace{O1 + O2 + O3 + O4 + O5 + O6 + O7 + O8 + O9}_{\text{TOTAL OUTPUT}}$$

Where:

- **I1** is the annual quantity of organic solvents or their quantity in mixtures purchased which are used as input into the process in the time frame over which the mass balance is being calculated. ***(Absolutely important quantity – must be determined as precisely as possible!)***
- **I2** is the annual quantity of organic solvents or their quantity in mixtures purchased which are recovered and reused as solvent input into the process. The recycled solvent is calculated every time it is used to perform any activity. ***(Relevant for calculation of total emission limit value as it is determined as the percentage of total solvent input I1 + I2.)***
- **O1** is the annual quantity of organic solvents emitted through the stacks. It represents the sum of VOC emitted from the VOC abatement equipment O1.1 (a clean waste gas) and VOC emitted from stacks without prior treatment O1.2. (Not relevant)
- **O2** are organic solvents lost in the water („waste water“) an annual level. If appropriate taking into account waste water treatment when calculating O5. ***(Not relevant, can be neglected)***
- **O3** is the solvent in product. The quantity of organic solvents which remains as contamination or residue in products output from the process an annual level. ***(Not applicable for production of coatings, varnishes, inks and adhesives)***
- **O4** are uncaptured emissions (fugitive emissions) of organic solvents to air. This includes the general ventilation of rooms, where air is released to the outside environment via windows, doors, vents and similar openings on an annual level. ***(To be calculated)***
- **O5** is the annual quantity of organic solvents and/or organic compounds lost due to chemical or physical reactions on annual level (including those which are destroyed, e.g. by incineration or other waste gas or waste water treatments, or captured, e.g. by adsorption, as long as they are not counted under O6, O7 or O8). ***(If there is no abatement unit, O5 is equal to 0!)***

- **O6** are organic solvents contained in collected waste an annual level. ***(Generally not very relevant for this type of production.)***
- **O7** are organic solvents, or organic solvents contained in mixtures that are sold or are intended to be sold as a commercially valuable product in a year. **(Absolutely important quantity – must be determined as precisely as possible!)**
- **O8** are solvents recovered but not as input into the process an annual level, if not classified as O7. ***(Generally not applicable to this type of production.)***
- **O9** are solvents released on an annual level in other ways (e.g. spillages). ***(Generally not relevant for this type of production.)***

As mentioned, using an annual solvent mass balance operator can do the following:

1. In line with the methodology defined in Article 6 and Annex 4 of the Regulation determine **Solvent consumption (SC)** as total input of organic solvents into an installation per calendar year, or any other 12-month period, from which any volatile organic compounds that are recovered for reuse are deducted.

SC = I1 – O8

Use solvent consumption to check whether Regulation applies to the installation (determine the status of VOC operator).

2. Perform **Compliance check** against emission limit values following these three simple steps:

Step 1: Calculation of total emission limit value

Total emission limit value [tonnes/year] = Annual Solvent input I (I1 + I2) x Percentage

where Percentage = 5% if I is between 100 and 1.000 tons/year
= 3% if I is > 1.000 tons/year

Step 2: Determination of total emissions by solvent mass balance

Total VOC emission (E) = Fugitive emission (F) + Captured emission in waste gas (O1),

E = F + O1,

if fugitive emissions (F) are calculated indirectly

F = I1 - O1 - O5 - O6 - O7 - O8

and

E= I1 – O5 – O6 – O7 – O8

Note: Fugitive Emission value does not include solvent sold as part of a coating preparation in a sealed container.

Step 3: Comparison of determined total emissions with emission limit value:

Compliance to requirements of Annex V, No 17, Regulation on VOC (Annex VII, Part 2, No 17, Industrial emissions Directive) is given as:

Determined total emission ≤ total emission limit value

Note: Compliance must be proven every year!

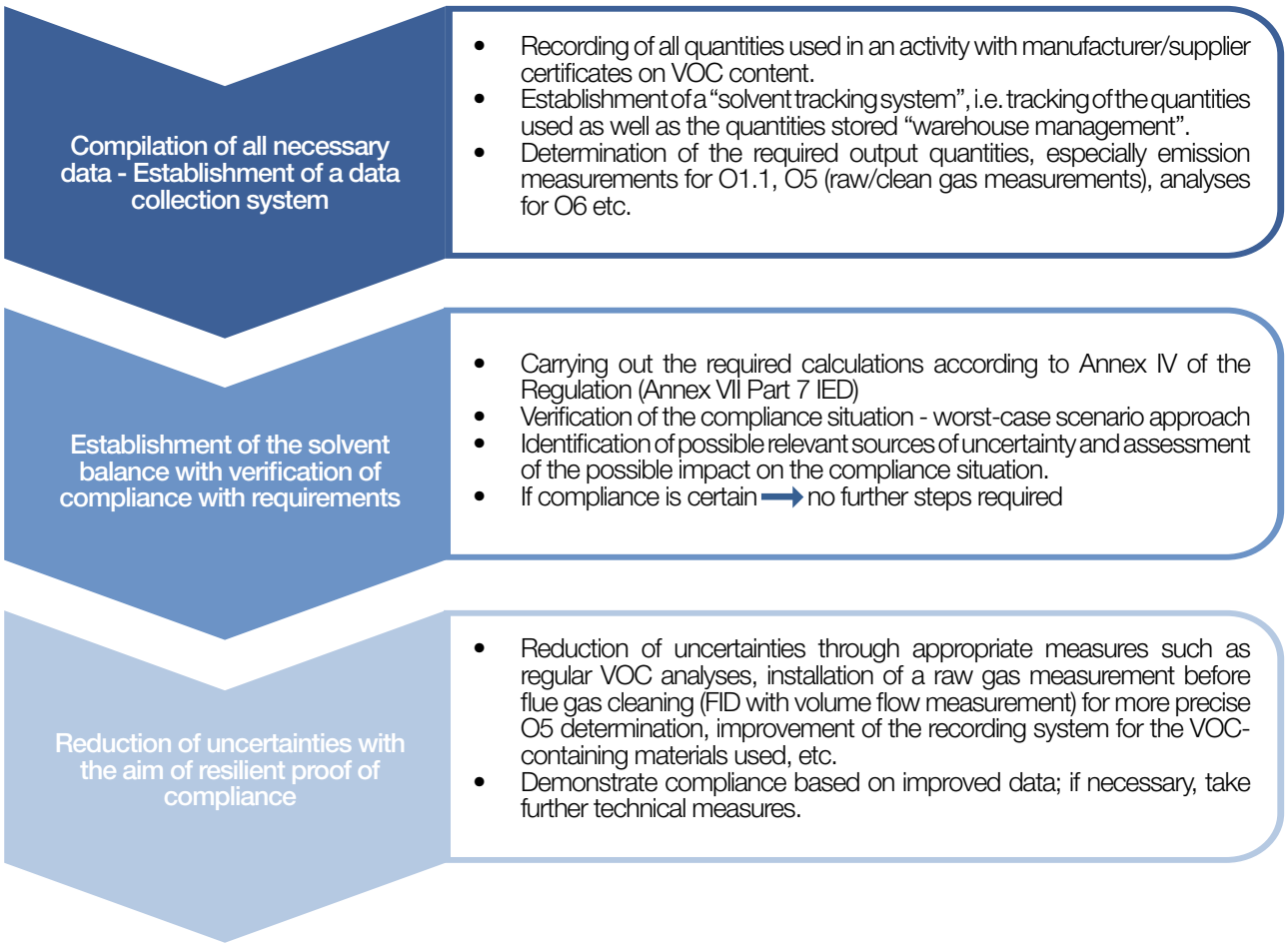
4 PRACTICAL PROBLEMS WITH SOLVENT MASS BALANCE

As can be seen from the description of the input/output flows, the solvent mass balance can be associated with considerable uncertainties. Therefore, the main objective is to represent the actual compliance for the respective activity as realistically as possible, by means of a high degree of accuracy in the input data.

During the elaboration of the solvent mass balance, some problems can frequently occur at the data collection, e.g.:

- Availability of purchasing quantities or consumption quantities.
- Information on VOC weight contents.
- The term "organic solvent" includes not only solvents but other volatile organic auxiliaries like softeners, too, that have to be considered in mass balance.
- Missing data on quantities of internal recovered solvents (e.g. by a distillation unit in installation).
- Uncertainties according to VOC content in produced paint, waste, waste gas, especially if waste gas volumes are fluctuating.

The figure below shows how this can best be done.



Goal: Reliable, verifiable solvent mass balance to prove compliance with the requirements of the Regulation, and respectively Chapter V IED

5 EXAMPLE

At the start of the year, a company has in stock 500 litres of solvent for thinning/cleaning and 1 000 litres of coating. The solvent has a density of 800 g/litre (0.8 kg/litre) and the coating contains 350 g/litre (0.35 kg/litre) of solvent. During the year, it purchases 6 000 litres of solvent and 10 000 litres of coating. At the end of the year, it has 700 litres of solvent in stock and 800 litres of coating.

Overall input I1 to the process: = Initial stock + Purchased stock – Final stock
= [(500 × 0.8) + (1 000 × 0.35)] + [(6 000 × 0.8) + (10 000 × 0.35)] – [(700 × 0.8) + (800 × 0.35)]
= 750 + 8 300 – 840 = 8 210 kg

Attention – the term "organic solvent" has a wide meaning and the volatility is referred even to the conditions of application

Regarding input I1 the question is how to calculate the VOC content of preparations with mixtures of several solvents.

Question: *What is the VOC content of a preparation such as a coating?*

Answer: *VOC is any organic compound having, at 293.15 K (20°C), a vapour pressure of 0.01 kPa or more, or having corresponding volatility under the particular conditions of use.*
In practice, many formulations falling under the scope of the Regulation on VOC such as paint, inks and adhesives will consist of a mixture of solvents, polymers and often other non-dissolved solids (e.g. pigments in coatings). The main problem for users is in understanding the VOC content of the preparation and hence being able to calculate their emissions and solvent mass balance.
It is virtually impossible for the formulator to predict or calculate the vapour pressure of the whole system they use, because of the complexity of physicochemical interactions between the components of the system, even when the vapour pressures of the pure raw materials are supplied by the manufacturers. Measurements of vapour pressures also present significant issues, in particular in regions below 0.1 kPa.
The best approach is to treat each solvent in the preparation individually. *The total VOC content of the system is related to mass percentages of VOC components in the formulation. Therefore, only individual compounds with a vapour pressure 0.01 kPa need to be considered.*
The formulator would need to identify which solvents have a vapour pressure over the 0.01 kPa limit (supplied by the solvent manufacturer), taking into account the temperature of use and document the VOC content of his formulation on this basis. *Components with a vapour pressure lower than 0.01 kPa would be excluded.*

An example of the calculation of the VOC content of a formulation:

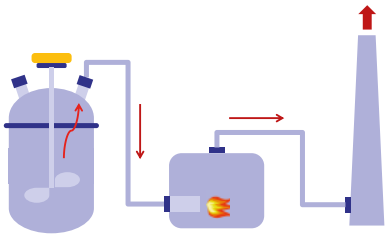
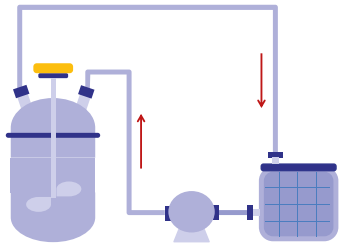
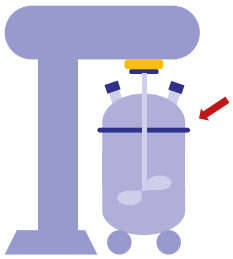
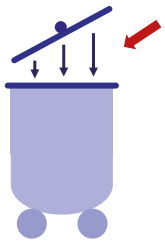
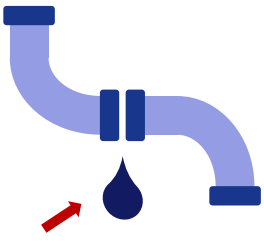
	Concentration, % (m/m)	Vapour pressure at 20°C, kPa
MEK	10	9.5
Xylene	10	1.5
Dearomatised Mineral Spirit 150/200	10	0.3
Butyl glycol	10	0.08
Butyl diglycol	10	0.007
Resin	50	< 0.001

For the calculation of the VOC content the concentrations of the components having a vapour pressure = 10 Pa should be considered (i.e. MEK, xylene, Mineral Spirit and butyl glycol all together 40% m/m). If the formulation was used at a temperature of 40°C then the value would be 50% m/m, because butyl diglycol would have a vapour pressure = 0.01 kPa at this temperature and should thus be included. Using the density of the preparation, the VOC content, expressed in g/l, can be calculated.
In Europe, the VOC content of a finished product, such as paint, is usually expressed in terms of grams of VOC per litre. In case the VOC content is expressed as the mass percentage of the paint (WVOC), conversion to grams per litre is done by using the following formula:

VOC = WVOC x DC / 100%	where: VOC = VOC content of paint (in g/L) WVOC = mass percentage of VOC components in paint (in % m/m) DC = density of paint at 20°C (in g/L)

6 APPLICATION OF BEST AVAILABLE TECHNIQUES

Application of Best Available Techniques allows the operators to reduce unwanted VOC emissions and improve the overall environmental performance of the installation. Presented techniques have been proven in practice to be effective in preventing or minimising emissions and impacts on the environment and to be economically viable. Among others they include the following:

	Establish a VOC solvent register for each recipe of paint so that you know exactly the solvent mass content of each product that you produce. Based on the solvent register the total quantity of sold VOC solvents in the products per year shall be determined with high precision.
	Keep the production system as closed as possible and prevent fugitive emissions – install extraction for VOC waste gases and discharge the VOC waste gases to appropriate waste gas abatement. All relevant containers and filling lines where VOC emissions can result should be connected to the VOC waste gas extraction line.
	VOC solvents should be transferred by pipes in a closed system from the storage containers to the dispensers, mixers etc. and not manually. Gas balance techniques should be applied during transfilling and loading/ unloading of VOC solvents.
	VOC fugitive emissions can be reduced by using high-end equipment like technical tight pumps, double mechanical sealed stirrer with controlled barrier medium (by monitoring of pressure) or magnetic driven stirrers, technical tight valves, flanges etc.
	Avoid open containers with VOC solvents by using covers with appropriate seals. Products should be stored in closed or covered containers. Waste solvent and used cleaning towels should be collected and stored in close containers.
	Leak detection and repair, as well as maintenance programs, should be applied. The personal staff should be trained and be aware of good housekeeping techniques.
	Apply low VOC emission cleaning techniques for the equipment e.g. using water-based cleaning agents and closed cleaning systems. Scheduling batches from light to dark colours also reduces the need for equipment cleaning. Pipes being used for different solvents or liquid material should be cleaned by installation of a pigging system.

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