HARRPA Hydrocarbon Resins, Rosin Resins and Pine Chemicals Producers Association

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HARRPA Statement on Volatile Organic Compounds

The issue

The products manufactured by the HARRPA (Hydrocarbon Resins, Rosin Resins and Pine Chemicals Producers Association) members are used in many applications, e.g. (hot melt) adhesives, rubber, chewing gum, cosmetics, paints, tyres and food contact applications. Usually the resins do not represent the major component of the article or material. More information on products can be found on the HARRPA website.

Indoor air quality becomes a real challenge for several Industry sectors. Indeed, within buildings or vehicle interiors several (semi) volatile organic chemical ((S)VOC) species can be detected which could influence the indoor air quality. Exposure to certain volatile organic chemical compounds, emitted from some materials used in indoor environment, can cause discomfort and impact Human health. For building and automotive Industries, for example, limitations in (S)VOC emissions are regulated. This is either based on (country specific) legislation or voluntary schemes. To characterise and quantify the regulated (S)VOCs and limits (both “in-can” and emission) different test methods are in use. However such testing methods are typically less suitable for direct measurement of tackifying resins, because they are not specifically designed for this product group: applying standard test procedures to tackifying resins could show unexpected peaks due to the fact that these products might be thermal unstable. In the assessment of the results this potential misclassification should be taken into consideration.

Tackifying resins manufactured by HARRPA members can be a component of compositions dedicated to building or automotive applications. It is difficult to estimate their potential impact on the results of (S)VOC tests evaluating composition dedicated to building and/or vehicle interior (such as adhesives, paints or coatings). This for the simple reason that HARRPA member products are typically formulated into final formulations by its customers. In addition, Hydrocarbon Resins

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and Rosin Resins manufacturers are not legally required to make any statement or claim regarding the (S)VOC emissions of their resins as supplied to their customers for further downstream use.

The purpose of this document is

a) to provide the position of HARRPA with respect to the discussion on Volatile Organic Compounds (VOC) at different stakeholder's levels and also to improve the VOC related technical discussion between suppliers and users,
b) to clarify resin manufacturers' opinion on their regulatory obligations, and,
c) to identify the use of resins and the applicable respective legislations (both at national and EU levels) and voluntary schemes.

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Statement on manufacturers' legal duties

At the date of the issue of this statement, it is HARRPA's understanding that:

- Hydrocarbon resins and rosin resins manufacturers are not legally required to make any statement or claim regarding either the VOC content or VOC emissions of their resins as supplied to their customers for subsequent downstream use.
- Current legal responsibilities for any declarations apply to those responsible for placing the final formulation or article containing the resins on the market.

In this respect Hydrocarbon resins and rosin resins manufacturers, for business purposes, may decide to communicate VOC related information to their customers on a voluntary basis.
More specific topics are reviewed in the various chapters of this paper.

Chapter 1 – VOC definitions & methods

Multiple (S)VOC definitions are in use. There is no harmonised (S)VOC definition used in the different regulations and (voluntary) requirements. Also, different definitions are in use for (S)VOC between assessment of emission (S)VOCs and (S)VOC content. In practice this could mean that a substance is identified as VOC under a certain regulation or requirement and identified as SVOC or non-VOC under another regulation or requirement. In the overview below a non-exhaustive overview is provided about the several (S)VOC definitions.

Main existing VOC and VOC-related definitions – all sectors are summarised in the following table.

Methods / Regulations	Classification of World Health Organization	EU Solvent Emissions Directive	International Standard ISO 16000-6	EC Directive 2004/42/EC	VDA 278 standard method
References (see last page)	*WHO Classification*	*EC Directive 1999/13/EC*	*International standard method*	*EU Regulation adapted in 2004*	*VDA-Recommendation ((German) Automotive standard)*
Scope of Method / Regulation	Categorization of chemical compounds to identify indoor VOCs and classify them into some classes	EU Regulation to prevent or reduce the direct and indirect effects of VOC emissions into the environment (into air and water)	Standard Protocol to determine of volatile organic compounds (VOCs) in indoor air	1- EU Regulation to identify the VOC and determine the VOC content for certain paints, varnishes and vehicle refinishing products 2- ISO 11890-2 referred method	Test procedure for non metallic materials used for moulded components in automotives enabling to measure VOC and FOG contents
Very Volatile Organic Compounds (VVOCs) definition	Boiling points range from <0°C to (50°C - 100°C)		Organic compounds eluting before n-hexane on a GC column specified as 5% phenyl / 95% methyl- polysiloxane phase capillary GC column		
Volatile Organic Compounds (VOCs) definition	Boiling points range from (50°C - 100°C) to (240°C - 260°C)	Organic compounds having at 293.15K a vapor pressure of 0.01 kPa (or more) or having a corresponding volatility under particular conditions of use	Organic compounds eluting between n-hexane and n-hexadecane on a GC column specified as a 5% phenyl / 95 % methyl polysiloxane phase capillary GC column	Any organic compound having an initial boiling point less than or equal to 250°C measured at a standard pressure of 101,3 kPa	Any organic compounds - with a boiling point in the range up to n-pentacosane (C25) - determined using thermal desorption at 90°C for 30 minutes. The emitted compounds are analyzed and calibrated using a toluene standard
Semi Volatile Organic Compounds (VOCs) definition	Boiling points range from (240°C - 260°C) to (380°C - 400°C)		Organic compound eluting after n-hexadecane on a gas chromatographic column specified as a 5 % phenyl 95 % methyl polysiloxane phase capillary gas chromatographic column		FOG (semi-volatile "fogging" compounds) correspond at any organic compounds - with a boiling point in the range of the C14 to C32 - determined using thermal desorption at 120°C for 60 minutes. The emitted compounds are analyzed and calibrated using a hexadecane standard

Chapter 2 - Current European/National Regulations and voluntary schemes on low VOC emissions for some applications

a) European regulations on low VOC emissions

a. Construction products

The Construction Products Regulation (CPR) is designed to ensure reliable information is given for construction products in relation to their performances. This is achieved by providing a “common technical language", offering uniform assessment methods of the performance of construction products. The Construction Products Regulation replaced the Construction Products Directive (CPD) in 2011. The Essential Requirements covered by the CPR are:

1. Mechanical resistance and stability
2. Safety in case of fire
3. Hygiene, health and the environment
4. Safety in use
5. Protection against noise
6. Energy, economy and heat retention
7. Sustainable use of natural resources

The emissions of dangerous regulated substances are covered under BWR33, and VOC emission is considered to be a regulated substance and so must be considered for compliance with the CPR. For the purposes of ‘regulated’, this is taken to mean any substance with an LCI (Lowest Concentration of Interest) and / or any hazardous substance.

Unlike other regulations, the CPR does not automatically cover all construction products. Individual CEN (product) technical committees are given a mandate by

the EU Commission, requiring them to issue a harmonised product standard laying down the CE marking requirements and the mandatory declaration of performance. Initially the mandates issued under the original CPR did not include a requirement to deal with BWR3 and until the mandates are revised, the current harmonized product standards generally do not cover emissions. As the existing mandates are amended, the CEN Technical Committees must amend the standards and explain how the products shall be tested for emissions, using the horizontally mandated test method developed by CEN TC351 (EN 16516-2017). As part of this process a VOC class scheme has been proposed, but has not yet been finalised or approved by the member states.

b. Paints Directive

The European "Paints" Directive (2004/42/EC) limits the total content of VOCs in some paints and varnishes, as well as in vehicle refinishing products, to reduce the VOC emissions leading to a reduction in the generation of ozone in the lower atmosphere. The next revision is assumed to include more product groups, but the expected revision timing remains unclear.

Any paint, varnish and vehicle refinishing product must not exceed the maximum VOC contents limit values as specified in the Directive. The limit values are for the ready to use product and the product must carry a label showing the type of product as given in the Directive, and the VOC contents (in g/l) of the product in a ready to use condition.

The VOC content is measured in Europe by direct injection into a gas chromatograph (ISO 11890-2; for VOC content between 0.01 and 100%). Reactive products are allowed to stand open for 1 hour after mixing before the test starts to allow initial curing. The VOC content is determined as total volatiles by monitoring weight loss during 1 hour heating at 110 °C (ISO 11890-1/ ISO 11890-2 depending on solvent content). In this ISO 11890-1 being a measurement of weight loss is not suited to be run on the neat tackifying resin due to inherent low VOC content of the tackifying resin. ISO11890-2, a measurement by GC, can be

considered however as described above take note that direct measurement on tackifying resins could show unexpected peaks. In the assessment of the results this potential misclassification should be taken into consideration. In both cases no subtraction of water or exempt compounds is performed. ISO 17895 can be used when VOC content is expected between 0.01 and 0.1%.

The VOC limits set in the Directive relate to the ready for use product. But tackifying resin suppliers have no obligation to comply with the Paints Directive. For practical reasons, the (maximum) VOC content of a product can be calculated by the final formulators.

The maximum VOC should be calculated based on any recommended additions of, for example, colorants and thinners. For this calculation data supplied by the raw material suppliers will be used: solids content, VOC content (based on VOC boiling point definition (≤ 250°C) or using similar ISO standards) and density, etc... For more details, please refer to the CEPE 'Guideline for VOC (Volatile Organic Compound) determination for the Decorative paint industry'.

In such cases and on a voluntary basis formulators and raw material suppliers may share information together (or via an external laboratory performing the evaluation (if necessary).

c. Harmonised Standard of EN 16516

By introducing the EN 16516 standard, EU Commission had the willingness to define an European Standard used to assign an emission class to show compliance with the several regulations and/or voluntary labels/schemes. This standard contains additional refinements for improving reliability. Also other valid information can be used as basis for this assignment of class, such as tests based on ISO 16000, but with shorter testing duration.

b) National regulations on VOC emissions

a. French VOC regulation

The French Decree (Regulation) was published on 25 March 2011 with details published on 13 May 2011 regarding a mandatory labelling of construction products installed indoors, floor and wall coverings, paints and lacquers with their emission classes based on emission testing.

The products covered currently by the French Decree are:

- Walls, ceiling, floor coverings and coatings,
- Panels for rooms partition and suspended ceiling
- Insulation products,
- Doors and windows,
- All products used for the installation of the products listed above.

The Decree came into effect on 1 January 2012 and means that any covered product placed on the market must be labelled with an emission class (A+, A, B, C) based on their emissions after 28 days, as tested with ISO 16000 and calculated for a European reference room (via EN 16516). Existing products had until September 2013 to comply with this. The emissions class will be assigned and self-declared by the manufacturer or the distributor. The label on the products includes a letter indicating the highest (worst) emissions class of the listed individual substances and the TVOC. There is no upper limit. Class C reflects performance higher than the limits for substances set by class B.

In addition to this regulatory requirement, the ANSES agency published a guideline (Protocole AFFSET5) for limiting VOC emissions into indoor air. This guideline should not be confused with the French regulation on VOC emissions described above. The AFSSET guideline is not a regulation but rather a non-binding guidance that may be used or not, depending on what the market requirements.

b. German VOC regulation

The German Ü mark for construction products is administered by German DIBt (German Institute for Construction Technology)/AgBB. It also highlights that the products in line with this German VOC Regulation for Building applications are conform to additional specifications in comparison with European CE marking. The Ü-mark is intended for all manufacturers or parties who wish to bring and use their construction products to the German market. Indeed, it indicates approval of usage of the construction product in Germany for products that are not covered by the harmonised European standards bearing the CE –marking.

c. Belgian VOC regulation

The Royal Decree establishing threshold levels for the emissions to the indoor environment was published on Aug 18, 2014. It covers:

- floor coverings,
- floor covering adhesives,
- surface coatings for wooden flooring.

The regulation has become mandatory on 1st January 2015 for products to be traded on the Belgian market for the first time. Manufacturers are responsible for ensuring that their products meet or fall below the limit values and are responsible for having the required product emission files available.
Approvals by an official body are not required nor is there an official label.
Laboratory tests have to be performed by an ISO 17024 accredited test lab following the new horizontally mandated European emission testing method EN 16516-2017.
The emissions are measured after 28 days but are more comprehensive for Belgium than the ANSES, German DIBt and AgBB measurement results can be used.

d. Swiss regulation (814.018)

Switzerland has a tax regulation for VOC's placed on the Swiss market. Certain products/substances fulfilling the criteria of the VOC definition in this tax regulation (organic compounds with a vapour pressure of at least 0.1 mbar at 20°C or a boiling point of maximum 240°C at 1013.25 mbar). Relevant substances and/or products are specified within Annex 1 and 2 of the regulation.

e. Voluntary Declaration schemes in Europe on low VOC emissions

In addition to regulatory requirements there are also voluntary schemes that manufacturers may wish to declare such as ecolabels and quality labels: e.g. EU-Ecolabel, EMICODE, GUT, Blue Angel, AgBB .

For details and requirements about these voluntary schemes see the respective websites of these labels.

Chapter 3 - Automotive industry and VOC emissions

a) Introduction

Air quality inside passenger cars becomes a real challenge for the world's automotive industry. Indeed, a lot of time can be spent within the indoor air compartment of vehicles. According to US and German studies on mobility, people can drive about 45 minutes per day (on average).

Vehicle interior can be considered as "relatively small volume, with variety of materials placed inside, including hard and soft plastics, adhesives, paints, lubricants and many others". All these materials can emit certain amounts of several volatile species, especially volatile organic compounds (VOCs) and semi-volatile organic compounds (SVOCs), throughout a vehicle's life. The latter can have an impact on vehicle interior air quality (VIAQ).

b) Regulations on vehicle interior air quality

Nowadays, no worldwide accepted regulation or guidelines regarding interior vehicle air quality has been defined. Some national automotive associations have developed their own guidelines that differ both in measured organic compounds number and their concentrations. The lists of prohibited VOCs differ from one regulation to another. Based on this observation, several standards regarding whole vehicle testing are used, and several car manufacturers control interior air quality of their vehicles via their own test methods. All these tests may create complexity to verify if (new) materials can reduce the emission of volatile organic compounds and improve air quality inside car cabins.

The International Organization for Standardization (ISO) has developed seven test procedures to characterise vehicle interior air quality under ISO 12219 standard. This standard could enable to harmonise the protocol for well characterizing VOC and SVOC released by materials inside car cabins while reducing their total content to an acceptable

level. The documents related to ISO 12219 standard describes normalised protocols for vehicle interior air quality based on simulation of three vehicle states deals (while including the specification for some organic compounds).

c) Potential test methods to characterise VOC and SVOC emission in car cabins

Car manufacturers wish (new) materials for car cabins that release low VOC levels. Without harmonising protocols to test vehicle interior air quality and several national regulations with their own list of VOCs (and limit concentration), each vehicle manufacturer can request specific tests to determine the impact of a new material on the air quality of car cabin.

The tackifying resins, manufactured by HARRPA members, are potentially incorporated in several materials dedicated to vehicle cabin. It is difficult to estimate their impact on the results of tests evaluating adhesives, paints or coatings dedicated to vehicle interior as these tackifying resins are used in formulations and not as such. In addition, Hydrocarbon Resins and Rosin Resins manufacturers are not legally required to make any statement or claim regarding the VOC emissions of their resins as supplied to their customers for further downstream use.

Some standard tests implemented by Automotive Industry may be performed on standard or new tackifying resins. By this way, their producers can establish the pattern of VOC and SVOC that could be emitted by their products. The emission behavior is typically analyzed by three main test methods in Automotive Industry: Odor testing, Fogging tests and VOC/SVOC determination.

d) Odor testing

One of main standards used to determine odor in automotive industry can be the German method called VDA 270, because organic compounds released from interior components can also be perceived as specific odors. The VDA 270 is suitable for controlling the odor perception of materials or formulations, as well as one component of one material or composition.

The sample is conditioned into a defined volume in a vessel on the basis of specific conditions (sample quantity, temperature and humidity). The air in the vessel is evaluated by three trained odor testers with an evaluation scale from 1 (not perceptible) to 6 (not acceptable).

In addition to the evaluation from VDA 270 standard, other OEM-specific evaluation schemes can be used to describe the odor in more detail. The protocol defined in ISO 12219-7 standard can be considered as an alternative to VDA 270 method.

e) Fogging test

Fogging test (DIN 75201, ISO 6452, SAE J1756) is also well known by car manufacturers, in particular to evaluate the tendency for plastic or elastomeric materials for volatizing substances that can condense on another surface. Two methods exist for Fogging Test:

- Photometric method determines the probability of a material to leave a light scattering film on a glass surface;
- Gravimetric method determines the content of volatile species from a material deposited onto an aluminum foil surface.

The principle of Fogging test is quite simple. The material (or the composition) which should be tested is heated in a glass beaker to evaporate some constituents. The volatized constituents of the material (or the composition) are condensed on a low temperature glass plate (photometric method) or a low temperature aluminum foil (gravimetric method). According to the method chosen, the results are obtained:

- for the photometric method: gloss readings of the glass cover before the test and after conditioning following the test are compared.
- for the gravimetric method: weights of the test sample and the aluminum foil before the test and immediately after the test are compared.

For a comparative analysis, it may be possible to test directly some tackifying resins or mixed in a simple formulation to check their effects on the result of fogging test.

f) VOC/SVOC determination

In general, the test methods used by Automotive Industry to characterize VOC and SVOC are useful to understand/interpret results of odor and fogging tests.

To characterise VOC/SVOC of materials (or compositions) and quantify them, a two-step process, called thermal desorption, is generally recommended. The first step involves placing the test sample in a clean, sealed vessel and heating it to simulate the emissions of VOCs in a hot car. The gases emitted from the sample in the test vessel are then collected and analysed for VOC/SVOC contents using gas chromatography / mass spectrometry (GC/MS) or high-performance liquid chromatography (HPLC) for aldehydes.

Two main thermal desorption methods are used by European car manufacturers:

- VDA 276 standard for VOC/SVOC analysis at the component level: the component is stored in a 1m3 emission chamber at a defined temperature and time. The organic compounds released are collected on Tenax-filled thermodesorption tubes and analysed using the thermodesorption GC/MS.
- VDA 278 standard for VOC/SVOC analysis at the material level: small amounts of material are placed directly in the thermodesorption tube, heated in the thermodesorber using a controlled temperature program; and the volatile (VOC) and semi-volatile (FOG) organic compounds released are analysed by using GC/MS device.

The VDA 278 method enables also to determine VOC and SVOC components released by some components of materials or compositions, such as polymers or tackifying resins. The data obtained in this case allow mainly to do comparative studies between several raw materials.

A third protocol for VOC/SVOC determination, named VDA 277 standard, can be recommended by some car manufacturers. This standard is based on Headspace GC/FID method to address the emission of organic compounds from non-metallic components,

such as plastics or adhesive compositions. By adapting this Headspace GC/MS analysis, it is possible to define the main individual emitted substances.

Chapter 4 - LCI[1] released by Joined Research Center (JRC) and other European Country regulations

- **Existing material emissions testing regulations in European Community:**

  ANSES French Regulation, AgBB / DIBT German Regulation[2], Belgian VOC Emissions Regulation, Spanish Regulation….

- **Construction product regulation[3]**
- **Following families of components are included in these LCI lists:**

  aromatic hydrocarbon, aliphatic and cyclic hydrocarbon, terpenes, aliphatic and aromatic alcohols, glycol, glycol ethers, glycol esters, aldehydes, ketones, acids, esters and lactones, halogenated / chlorinated hydrocarbons, others, ...

- **LCI can be very different from one regulation to the others:**

  Generally related to the timing of the LCI determination to update regulations.

  LCI equivalence between different regulation still varies quite significantly but AgBB/DIBT recently aligned with many EU-LCI values

  Future European regulations will hopefully harmonise LCI existing in the various country regulations into the (agreed) EU-LCI values.

[1] https://publications.jrc.ec.europa.eu/repository/handle/JRC114593
[2] http://www.umweltbundesamt.de/sites/default/files/medien/355/dokumente/agbb_evaluation_scheme_2015.pdf
[3] http://ec.europa.eu/growth/sectors/construction/product-regulation/index_en.htm

- VOC for Indoor air is related to the final formulation:
  - Contribution of Raw Material (=RM) to final VOC compounds depends on RM% in the final formulation and production process parameters.
  - In AgBB / DIBT and Afsset, the acceptable LCI of compounds can be linked to the sum of single identified components LCI when these single components have an identified LCI.
  - EN 16516-2017 seems to be a real improvement and is presented as replacement for other standards.

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- EPA Technical overview of Volatile Organic Compounds (available on https://www.epa.gov/indoor-air-quality-iaq/technical-overview-volatile-organic-compounds)