INTERNATIONAL DOCTORAL
SCHOOL OF THE USC

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PhD Thesis

DEFINING THE MOST ECO-EFFICIENT VEHICLE PAINT SHOP IN VIEW OF FORMALDEHYDE EMISSIONS PERFORMANCE

Santiago de Compostela, 2023

Doctoral Programme in Chemical and Environmental Engineering

ESCOLA DE DOUTORAMENTO
INTERNACIONAL DA USC

TESE DE DOUTORAMENTO

DEFINING THE MOST ECO-EFFICIENT VEHICLE PAINT SHOP IN VIEW OF FORMALDEHYDE EMISSIONS PERFORMANCE

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Acknowledgements

I would like to use these lines to express my gratitude to all those people who helped me directly or indirectly in the completion of my doctoral thesis.

First and foremost, I am indebted to Dr. Renate Adam, Manager of the Environmental Compliance and Sustainability department and my supervisor at the company Opel. She gave me the opportunity to conduct this work and provided me with support, advise and understanding throughout all these years. I would also like to thank her for the dedicated time and contribution in the publication of the research article on the LCA of the painting process.

I also wish to thank my supervisors at the University, Prof. Dr. Francisco Omil and Prof. Dr. Gumersindo Feijoo, who offered me the excellent chance to carry out this thesis at their research group. I am very grateful for their guidance and supervision during this long and arduous journey. I very much appreciate their flexibility in finding time to answer my questions and correct my work.

I am particularly thankful for the collaboration of Aida García Muñoz, who performed her master thesis under my supervision at the company. Her contribution made possible the elaboration of the chapters on LCA and eco-efficiency. I also thank Dr. Ana Arias Calvo for her advice on the publication of the mentioned research article and on the organizational issues related to the thesis submitting process, and my former colleague and friend Dr. Jorge Bordello, who shared his research journey with me during my first “doctoral life” at the University. The memories of that time motivated me to accomplish this objective.

I would like to thank my colleagues at Opel and all company engineers and specialists that helped me in some way in the development of this work.

I do not forget to thank the most important people in my life. My mother Isabel, for her unconditional support and understanding. She is largely responsible for who I am today. A special mention to my father José Ángel, who sadly passed away last year. I know that, in one way or the other, he accompanies me and gives me strength to achieve my goals. My wife Martina, who not only shares her life with me but also fills mine with happiness and love. Without her help and encouragement, I would not have been able to finalize this work. Finally, my daughters Lúa and Soley, who are the reason I get up every day (in every sense). I am thankful for each minute I spend with them. They could not make me happier and prouder.

Last but not least, thanks to the rest of my family and friends who are and were with me in the difficult moments.

Thank you.

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Abbreviations

ALO	Agricultural Land Occupation
BC	Basecoat
BiW	Body in White
BREF	Best Available Techniques Reference Document
CC	Clearcoat (chapter 1)
CC	Climate Change (all other chapters)
CLP	Regulation on classification, labelling and packaging of substances and mixtures
COD	Chemical Oxygen Demand
CP	Cavity Preservation (wax)
DNPH	2,4-Dinitrophenylhydrazine
EC	Electrocoating
ELV	Emission Limit Value
EU	European Union
FD	Fossil Depletion
FE	Freshwater Eutrophication
FET	Freshwater Ecotoxicity
HPLC	High-Performance Liquid Chromatography
HT	Human Toxicity
IR	Ionizing Radiation
JPH	Jobs Per Hour
LCA	Life Cycle Assessment
LCI	Life Cycle Inventory
LCIA	Life Cycle Impact Assessment
MD	Metal Depletion
ME	Marine Eutrophication
MET	Marine Ecotoxicity
MSDS	Material Safety Datasheet
NLT	Natural Land Transformation
OD	Ozone Depletion
PHO	Phosphating
PMF	Particular Matter Formation
POF	Photochemical Oxidant Formation

PR	Primer application
PT	Pretreatment
PT-EC	Pretreatment and Electrocoating
PVC	Polyvinyl Chloride
RTO	Regenerative Thermal Oxidizer
SB	Solvent based coating.
SB'1k	Solvent based one-component
SD	Sealing and dumping
S1	System 1
SS1	Subsystem 1
SS2	Subsystem 2
SS3	Subsystem 3
STS	Surface Treatment Using Organic Solvents
TA	Terrestrial Acidification
TC	Topcoat (Basecoat + Clearcoat)
TET	Terrestrial Ecotoxicity
TOC	Total Organic Carbon
ULO	Urban Land Occupation
VOC	Volatile Organic Compound
WB	Water based
WD	Water Depletion
WWTP	Wastewater Treatment Plant

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RESUMO

A clasificación de substancias e mesturas revísase e corríxese continuamente na Unión Europea para reflectir as adaptacións ao progreso técnico e científico. Por tanto, a clasificación dos produtos químicos actualízase periodicamente e novas substancias poden reclasificarse como perigosas. O formaldehído foi reclasificado en 2015 como unha substancia cunha categoría canceríxena máis alta, recibindo as Frases de Perigo H350, *pode provocar cancro*, e o H341, *sospeitoso de provocar defectos xenéticos*. Por conseguinte, todas as industrias contempladas na Directiva 2010/75/UE sobre as emisións industriais substituirán, na medida do posible, o formaldehído por substancias menos perigosas. Ademais, se non poden evitarse as emisións desta substancia, debe respectarse un valor límite de emisións significativamente máis estrito de 2 mg/m^3 nos seus focos de emisión.

Un dos sectores industriais afectados pola reclasificación do formaldehído é a industria do automóbil, e en particular as operacións de pintado de vehículos debido á presenza de resinas de melamina na composición das pinturas. Este cambio obrigou aos fabricantes de vehículos a avaliar a súa situación legal e aplicar medidas técnicas e operativas para reducir ou eliminar as emisións de formaldehído.

O proxecto desta tese de doutoramento industrial é parte da investigación en curso que a empresa Opel (en adiante "a empresa") está a levar a cabo para recoñecer e identificar a tempo a reclasificación dos produtos químicos utilizados nos seus procesos e avaliar os seus impactos ambientais e económicos. Neste contexto, a empresa debía avaliar o impacto do mencionado cambio na clasificación de perigo do formaldehído con respecto ao cumprimento da lexislación ambiental e as súas repercusións económicas. Para ese efecto, levou a cabo un estudo detallado en diferentes plantas de produción de vehículos. Este estudo incluíu a avaliación do cumprimento do valor límite legal de emisión aplicable mediante medicións das concentracións de formaldehído nas chemineas dos procesos de pintado afectados, unha avaliación das posibilidades para reducir ou eliminar as emisións de formaldehído, incluíndo a substitución de materias primas e a instalación de equipos de redución de gases residuais, e un estudo económico das diferentes posibilidades. Como pasos esenciais deste traballo, levouse a cabo unha análise de ciclo de vida (ACV) do proceso de pintado nunha planta real de pintura de vehículos e unha análise de ecoeficiencia das diferentes alternativas para reducir as emisións de formaldehído. Os resultados e coñecementos recolleitos nesta investigación permitiron presentar unha proposta sobre a planta de pintura de vehículos máis ecoeficiente considerando o impacto das emisións de formaldehído.

Esta tese doutoral dividiuse en varios capítulos que abordan os principais obxectivos do proxecto. Nas seccións seguintes resúmese brevemente o contido de cada capítulo, así como as metodoloxías aplicadas e os principais resultados e conclusións obtidos.

Capítulo 1. Introdución: Marco deste traballo

O capítulo 1 é un capítulo introdutorio que contextualiza o marco desta tese. En primeiro lugar, descríbese a empresa na que levou a cabo este traballo. A isto séguelle unha explicación da *estado da arte* dos procesos de pintado de vehículos, que é o resultado dunha investigación bibliográfica e a visita e avaliación das plantas de pintura sobre a base da información proporcionada por enxeñeiros e operadores da empresa. Con esta información, introdúcense as plantas de pintura da empresa e móstranse as súas particularidades. Por último, descríbense o problema das emisións de formaldehído que xorde nas plantas de pintura de vehículos debido á mencionada reclasificación e as principais opcións para reducir ou eliminar as emisións de formaldehído.

A empresa Opel conta con dez fábricas, seis das cales se dedican á produción de vehículos. O proceso de produción do vehículo lévase a cabo en diferentes zonas onde se producen, ensamblan e pintan a maioría das partes do vehículo. As catro áreas principais involucradas no proceso de produción son: taller de prensas, taller de carrocerías, taller de pintura e taller de montaxe final. En particular, as operacións de pintado realizadas no taller ou planta de pintura causan os maiores impactos ambientais de todo o proceso de produción. A alta demanda de enerxía e recursos materiais, o consumo de auga, a xeración de residuos e augas residuais, así como a emisión á atmosfera de compostos orgánicos volátiles (COV) son os aspectos ambientais máis significativos dos procesos de pintado.

O proceso de pintado de vehículos consiste nunha secuencia de procesos de inmersión, así como na aplicación de pinturas e materiais de recubrimento utilizando equipos de atomización. Os pasos principais no proceso de pintado son pretratamiento, cataforese, selado de PVC, capa de imprimación, capa de pintura base e capa de laca clara ou verniz. As diversas capas aplicadas nestas etapas garanten unha protección a longo prazo contra a corrosión, as condicións meteorolóxicas, a influencia química, etc.

As distintas capas aplicadas na carrocería do vehículo conséguense aplicando recubrimentos e pinturas con diferentes compoñentes e aditivos que lles proporcionan a estabilidade, durabilidade e características visuais necesarias. En xeral, os compoñentes básicos das pinturas son os disolventes orgánicos, a auga, as resinas, os plastificantes, as tinguiduras e os pigmentos. Unha das resinas máis usadas nas pinturas dos vehículos son as resinas de melamina, producidas pola reacción de melamina e formaldehído. Por tanto, o formaldehído está presente nas pinturas para automóbiles como residuo asociado ao proceso de fabricación da resina, pero tamén como compoñente ligado aos polímeros de melamina.

Tendo en conta a presenza de formaldehído nas pinturas dos vehículos e a súa alta volatilidade, caben esperar emisións desta substancia á atmosfera. Neste capítulo establécese a hipótese sobre as áreas e procesos nos que poden producirse emisións de formaldehído. A hipótese pode resumirse da seguinte maneira:

- En primeiro lugar, unha pequena cantidade de formaldehído libre presente nas pinturas pode emitirse á atmosfera a través dos gases residuais procedentes directamente das cabinas de pintado.

- En segundo lugar, a estrutura melamina-formaldehído rómpese durante o proceso de curado de pintura dentro dos fornos de secado a altas temperaturas, liberando formaldehído que se emitirá á atmosfera se non se instala ningún equipo de redución de emisións ou se o sistema de redución non é capaz de eliminar o formaldehído.

Esta hipótese analízase a fondo no capítulo 2.

As seis plantas de pintura da empresa foron consideradas neste traballo para a avaliación das emisións de formaldehído. Levouse a cabo unha avaliación exhaustiva de cada planta como etapa preparatoria para o estudo realizado no capítulo 2. No capítulo 1 indícanse as diferentes características e condicións de traballo de cada planta.

En canto ás opcións para reducir ou eliminar as emisións de formaldehído, faise unha distinción entre as emisións de formaldehído libre das cabinas de pintado e as emisións dos fornos de secado. En canto á primeira, a purificación das pinturas para reducir a concentración de formaldehído libre é a medida máis adecuada. A opción elixida polos fabricantes de pintura foi mellorar os procesos de fabricación da resina para eliminar as impurezas do formaldehído. Para eliminar ou reducir as emisións de formaldehído dos fornos de secado, pódense considerar dúas tecnoloxías alternativas. A primeira opción é a instalación dun oxidador térmico rexenerativo (RTO en inglés). Este equipo consta de varios leitos con recheo cerámico onde o proceso de oxidación ten lugar nunha serie de pasos alternos de quecemento e arrefriado. A segunda alternativa é a oxidación térmica recuperativa, que consiste nunha cámara de combustión única na que se produce a oxidación dos COV. Ambos tipos de tecnoloxía poden tratar todos os gases residuais dos fornos de secado e baséanse nos principios da oxidación térmica. As características de cada tecnoloxía explícanse no capítulo 1.

Capítulo 2. Inventario das emisións de formaldehído

No capítulo 2 descríbese a primeira investigación realizada nas seis plantas de pintura de vehículos da empresa en relación coas medicións das emisións de formaldehído. Neste capítulo explícanse a elaboración dos programas de medición e as metodoloxías aplicadas para as medicións. Posteriormente, examínanse e expóñense os resultados tendo en conta a hipótese enunciada no capítulo 1. Identifícanse as plantas de pintura e os procesos que requiren medidas correctivas para garantir o cumprimento do valor límite de emisión aplicable e propóñense medidas específicas para a redución das emisións de formaldehído. Por último, móstranse os datos de inventario das emisións de formaldehído utilizados para a análise de ciclo de vida (ACV) desenvolto no capítulo 3.

Para realizar as medicións das concentracións de formaldehído, elaboráronse programas de medición específicos para cada planta de pintura. Seleccionáronse e incluíron nos programas as chemineas pertinentes dos procesos afectados. En xeral, o alcance das medicións incluíu os gases residuais das cabinas de pintado, as zonas de *flash off* e os fornos de secado dos subprocesos de cataforese, imprimación, capa de pintura base e capa de laca clara. En casos específicos, tamén se incluíron os gases residuais procedentes de operacións menores como o selado de PVC ou a aplicación de ceras. Neste capítulo indícanse os puntos de medición específicos de cada planta, así como as condicións de funcionamento durante a mostraxe.

As medicións leváronse a cabo por empresas de medición dispoñibles na rexión onde se atopa a planta de produción. Estas empresas foron seleccionadas tras un exame preliminar que asegurou que contasen coa acreditación e os coñecementos necesarios para a mostraxe e a análise das medicións das emisións de formaldehído. As empresas aplicaron tres metodoloxías diferentes (*DNPH Method – Impinger Method, XAD-2 Collection Tubes Method and*

Multicomponent FTIR Gas Analyzer), en función da súa dispoñibilidade e acreditación. Estas metodoloxías descríbense en detalle neste capítulo.

Os resultados das medicións confirman e validan a hipótese enunciada no capítulo 1. As concentracións observadas nos gases residuais das cabinas de pintado en todas as plantas foron tipicamente inferiores a 0.5 mg/m^3 e, por tanto, moi inferiores ao valor límite de emisión aplicable. Isto indica que as emisións das cabinas non son motivo de preocupación desde o punto de vista legal. Pola contra, as concentracións atopadas á saída dos fornos de secado superan significativamente o valor límite de emisión, con resultados que alcanzan 88.3 mg/m^3. Os resultados tamén demostran que as altas concentracións de formaldehído despois do forno poden reducirse con éxito a valores inferiores ao valor límite de emisión aplicable se se instala un equipo de redución para tratar o gas residual do forno e este opérase correctamente. As dúas tecnoloxías consideradas, é dicir, a oxidación térmica rexenerativa e recuperativa, puideron reducir o formaldehído obtendo resultados similares.

Tendo en conta estes resultados, propóñense medidas correctivas para reducir as emisións de formaldehído en dúas plantas nas que se observaron concentracións elevadas. Estas accións inclúen o aumento da temperatura de operación de 540 °C a 730 °C nos sistemas de redución de emisións dos fornos de imprimación, a redirección dos gases da zona de *flash off* de imprimación para ser tratados nos devanditos sistemas de redución, a reparación ou a substitución de pezas danadas e equipos de redución antigos para lograr unha eficiencia de destrución adecuada, e a instalación de equipos de redución de emisións nos fornos do proceso de acabado (capa de pintura base e laca clara) cuxos gases residuais emítense á atmosfera sen tratamento.

Como seguinte paso, levouse a cabo unha avaliación dos impactos ambientais e económicos das diferentes accións nunha das dúas plantas de pintura afectadas. Para iso realizouse un ACV do proceso de pintado nesta planta e unha análise de ecoeficiencia das diferentes opcións para reducir o formaldehído. Os resultados obtidos na planta de pintura estudada utilizáronse para elaborar o inventario para estas análises. Ambos estudos descríbense nos capítulos 3 e 4.

Capítulo 3. Análise de Ciclo de Vida

O capítulo 3 ocúpase do ACV do proceso de pintado de vehículos nunha planta de pintura na que se observaron altas emisións de formaldehído. Esta avaliación realizouse para analizar os impactos ambientais do proceso e comparar estes impactos antes e despois da introdución das diferentes accións para reducir as emisións. Para levar a cabo este estudo, definíronse diferentes escenarios que se describen en detalle neste capítulo.

Seguindo a definición dos escenarios, explícanse e móstranse as metodoloxías empregadas tanto para o ACV como para a elaboración do Inventario de Ciclo de Vida (ICV) necesario. Por último, examínanse os resultados da análise, o que permite comparar os distintos escenarios en relación co seu impacto ambiental.

Os escenarios estudados no ACV poden resumirse da seguinte maneira:

- Caso Base: representa a planta de pintura como funcionaba en 2015 antes de que se implementase calquera acción para reducir as emisións de formaldehído.
- Escenario A: representa a planta de pintura en 2016 despois de que se implementou un primeiro conxunto de accións. Éstas consisten nunha redución da cantidade de

formaldehído libre nas pinturas e unha diminución das emisións do proceso de imprimación mediante a introdución de melloras técnicas e operativas.

- Escenario B: considera a planta de pintura no Escenario A coa instalación adicional dun RTO para tratar os gases residuais dos fornos de acabado (2018).
- Escenario C: é unha alternativa ao Escenario B que implica a instalación de varios oxidadores térmicos recuperativos en lugar do RTO para os gases residuais dos fornos de acabado (2018).
- Escenario D: representa a planta de pintura no Escenario B coa adición dunha futura mellora. Esta mellora consiste nun tratamento completo das emisións das cabinas de aplicación da capa de pintura base.

Con respecto á metodoloxía, realizouse un ACV atribucional do proceso de pintado na planta de pintura estudada desde unha perspectiva “do berce á tumba", seguindo os requisitos e directrices das normas ISO 14040:2006 e ISO 14044:2006. Para levar a cabo o ACV, realizouse unha Análise de Impacto de Ciclo de Vida (AICV) utilizando o software comercial SimaPro v.8.2 coa metodoloxía European ReCiPe Midpoint V1.12, utilizando a base de datos EcoInvent v3.2. Esta metodoloxía ten en conta 18 categorías de impacto.

Para a elaboración do ICV, recompiláronse datos sobre o consumo de materiais e enerxía, así como datos de residuos e emisións correspondentes a un ano de produción, e refiríronse á unidade funcional dunha hora de funcionamento. No presente capítulo móstranse os datos de inventario recompilados para os subprocesos incluídos no estudo (cataforese, imprimación, pintura base e laca clara).

Tras a selección das categorías de impacto e a clasificación dos resultados do inventario, seguíronse os pasos de caracterización e normalización definidos nas normas ISO mencionadas. A caracterización do proceso de pintado no Caso Base realizouse para identificar o subproceso con maior impacto ambiental. Ademais, realizouse a caracterización de cada un dos subprocesos para recoñecer os *inputs* e *outputs* que contribúen en maior medida ao impacto ambiental. O seguinte paso foi a caracterización do sistema para os Escenarios A, B e C, e finalmente o Escenario D.

A continuación, para facilitar a comparación dos distintos escenarios, normalizáronse os resultados. Para comparar os datos normalizados, aplicáronse dous criterios diferentes na selección das categorías de impacto máis relevantes:

- Todas as categorías de impacto cuxa contribución relativa ao impacto ambiental total foi superior ao 2 %.
- Toxicidade humana (HT en inglés) exclusivamente.

Os resultados da caracterización do proceso de pintado no Caso Base indican que o proceso de acabado (pintura base e laca clara) causa os maiores impactos ambientais de todo o proceso. Este resultado é razoable debido ao maior consumo de materiais e á produción de emisións deste subproceso, ao maior consumo de gas natural e ás emisións directas sen sistemas de redución instalados. Ademais, a cataforese tamén se identificou como un proceso cunha contribución relevante ao impacto ambiental total, principalmente debido á resina epoxi contida na pasta catiónica utilizada neste proceso.

Unha vez analizado o proceso completo de pintado, avaliáronse os escenarios de mellora definidos. Os resultados de caracterización do Escenario A comparáronse cos do Caso Base.

No proceso de imprimación observouse unha diminución do 7 % da categoría de impacto de toxicidade humana (HT). Por tanto, o Escenario A logra reducir a toxicidade humana mediante a redución das emisións de formaldehído. Con todo, o maior consumo de gas natural deste escenario debido ao aumento da temperatura de operación dos equipos de redución de emisións conduciu a un aumento en case todas as demais categorías de impacto.

Tras a análise do Escenario A, estudáronse os Escenarios B e C. Observouse que ambas as tecnoloxías de redución avaliadas nestes escenarios lograron unha diminución da toxicidade humana debido á redución das emisións de formaldehído. Con todo, a instalación de oxidadores térmicos recuperativos (Escenario C) alcanzou unha redución da toxicidade humana máis significativa que o RTO (Escenario B). Por outra banda, os oxidadores recuperativos lograron unha mellora xeral ao considerar as categorías de impacto máis relevantes seleccionadas neste estudo, a diferenza do RTO, que produce un aumento do impacto ambiental. Estes resultados explicáronse polo maior consumo total de enerxía da tecnoloxía de oxidación térmica rexenerativa. Por tanto, a instalación dos oxidadores térmicos recuperativos é a alternativa máis sostible desde o punto de vista ambiental.

Por último, analizouse o Escenario D. Este escenario non logrou unha redución da categoría de impacto de HT. A mellora da HT causada pola redución das emisións de COV e formaldehído das cabinas de aplicación da pintura base compénsase cunha deterioración debida ao aumento do consumo de gas natural.

Os resultados obtidos no ACV confirmaron que todos os escenarios estudados lograron reducir a toxicidade humana se se comparan coa situación inicial da planta de pintura. Con todo, a magnitude desta redución é diferente para os diferentes escenarios. A aplicación consecutiva do Escenario A seguida do Escenario C representa a opción máis sostible desde o punto de vista do medioambiente, tanto en vista da toxicidade humana como do impacto ambiental total.

Capítulo 4. Análise de Ecoeficiencia dos equipos de redución de emisións de formaldehído

O aspecto económico non se incluíu na avaliación do capítulo 3. Co fin de proporcionar á empresa información adicional para a toma de decisións e seleccionar a tecnoloxía máis adecuada para a redución das emisións dos fornos de acabado, levouse a cabo unha avaliación económica e unha análise de ecoeficiencia. Estas avaliacións descríbense no capítulo 4. A metodoloxía empregada para a análise así como a interpretación dos resultados obtidos figuran no presente capítulo. En base a estes resultados, explícase e xustifícase a decisión final da empresa. En última instancia, neste capítulo preséntase unha proposta para a planta de pintura de vehículos máis ecoeficiente considerando o impacto das emisións de formaldehído.

A avaliación económica e a análise de ecoeficiencia realizáronse para comparar as dúas opcións de redución das emisións dos fornos de acabado na planta de pintura estudada no capítulo 3. Na avaliación económica, recompiláronse todos os datos de custos necesarios para realizar a análise de ecoeficiencia. Estes datos inclúen os custos de instalación, funcionamento e mantemento dos dous sistemas de redución ao longo da súa vida útil. Os custos totais normalizáronse á unidade funcional para permitir a comparación entre os dous sistemas. A análise de ecoeficiencia realizouse sobre a base dos criterios prescritos na norma ISO 14045:2012.

Para a análise de ecoeficiencia utilizáronse os resultados de normalización obtidos previamente no ACV. Seleccionáronse dous indicadores diferentes, que se compararon co custo total por hora:

- Variación do índice normalizado, expresada en porcentaxe, considerando a suma das categorías de impacto cunha contribución relativa ao impacto ambiental total superior ao 2 % nos resultados da normalización.
- Variación do índice normalizado, expresado en porcentaxe, da categoría de impacto HT.

Os resultados da avaliación económica figuran no presente capítulo. As diferenzas significativas nos custos totais dos dous sistemas foron explicadas. Os resultados da análise de ecoeficiencia demostran que, nos casos en que só se persegue a redución das emisións de formaldehído para garantir o cumprimento legal, xunto cunha mellora xeral da toxicidade humana, e os custos son o principal factor no proceso de toma de decisións, o RTO é a opción de redución de emisións máis favorable desde o punto de vista económico. Os custos totais para a instalación dos oxidadores térmicos recuperativos son 2.2 veces superiores aos do RTO (305.36 €/h e 136.85 €/h, respectivamente). Por tanto, a decisión da empresa de instalar un RTO nos fornos de acabado da planta de pintura estudada puideron xustificarse por estes resultados.

Os resultados e coñecementos adquiridos nesta tese doutoral permiten facer unha proposta para a planta de pintura de vehículos máis ecoeficiente considerando o impacto das emisións de formaldehído. Esta proposta preséntase no capítulo 4 como resultado principal deste traballo. En particular, cando se trata da redución das emisións de formaldehído dos fornos de acabado, propúxose a instalación de oxidadores térmicos recuperativos como a mellor opción, diminuíndo á súa vez a pegada ambiental da planta de pintura.

Conclusións xerais

Esta tese de doutoramento industrial tiña como principais obxectivos comprender exhaustivamente as emisións de formaldehído nas plantas de pintura das fábricas de produción de vehículos desde unha perspectiva ambiental e legal, propoñer e avaliar diferentes posibilidades de redución ou eliminación destas emisións e, en última instancia, formular unha proposta para a planta de pintura de vehículos máis ecoeficiente considerando o impacto das emisións de formaldehído. Os resultados obtidos no capítulo 2 en relación coas medicións das emisións de formaldehído en seis plantas de pintura, no capítulo 3 mediante unha Análise de Ciclo de Vida e, por último, no capítulo 4 mediante a avaliación económica e a análise de ecoeficiencia, permitiron alcanzar estes obxectivos.

Os resultados deste traballo proporcionan nova información aos fabricantes de vehículos e aos operadores das plantas de pintura, facilitando o proceso de toma de decisións na selección da tecnoloxía de redución de emisións de gases residuais máis adecuada e outras medidas para a redución ou eliminación das emisións de formaldehído.

Neste traballo, confirmáronse o ACV e a análise de ecoeficiencia como ferramentas poderosas que poden ser aplicadas no sector industrial durante as actividades de planificación e selección para avaliar e identificar a tecnoloxía máis sostible desde o punto de vista ambiental.


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RESUMEN

La clasificación de sustancias y mezclas se revisa y corrige continuamente en la Unión Europea para reflejar las adaptaciones al progreso técnico y científico. Por lo tanto, la clasificación de los productos químicos se actualiza periódicamente y nuevas sustancias pueden reclasificarse como peligrosas. El formaldehído fue reclasificado en 2015 como una sustancia con una categoría cancerígena más alta, recibiendo las Frases de Peligro H350, *puede provocar cáncer*, y el H341, *sospechoso de provocar defectos genéticos.* Por consiguiente, todas las industrias contempladas en la Directiva 2010/75/UE sobre las emisiones industriales sustituirán, en la medida de lo posible, el formaldehído por sustancias menos peligrosas. Además, si no pueden evitarse las emisiones de esta sustancia, debe respetarse un valor límite de emisiones significativamente más estricto de 2 mg/m^3 en sus focos de emisión.

Uno de los sectores industriales afectados por la reclasificación del formaldehído es la industria del automóvil, y en particular las operaciones de pintado de vehículos debido a la presencia de resinas de melamina en la composición de las pinturas. Este cambio obligó a los fabricantes de vehículos a evaluar su situación legal y aplicar medidas técnicas y operativas para reducir o eliminar las emisiones de formaldehído.

El proyecto de esta tesis de doctorado industrial es parte de la investigación en curso que la empresa Opel (en adelante "la empresa") está llevando a cabo para reconocer e identificar a tiempo la reclasificación de los productos químicos utilizados en sus procesos y evaluar sus impactos ambientales y económicos. En este contexto, la empresa debía evaluar el impacto del mencionado cambio en la clasificación de peligro del formaldehído con respecto al cumplimiento de la legislación medioambiental y sus repercusiones económicas. A tal efecto, se llevó a cabo un estudio detallado en diferentes plantas de producción de vehículos. Este estudio incluyó la evaluación del cumplimiento del valor límite legal de emisión aplicable mediante mediciones de las concentraciones de formaldehído en las chimeneas de los procesos de pintado afectados, una evaluación de las posibilidades para reducir o eliminar las emisiones de formaldehído, incluyendo la sustitución de materias primas y la instalación de equipos de reducción de gases residuales, y un estudio económico de las diferentes posibilidades. Como pasos esenciales de este trabajo, se llevó a cabo un análisis de ciclo de vida (ACV) del proceso de pintado en una planta real de pintura de vehículos y un análisis de ecoeficiencia de las diferentes alternativas para reducir las emisiones de formaldehído. Los resultados y conocimientos recogidos en esta investigación permitieron presentar una propuesta sobre la planta de pintura de vehículos más ecoeficiente considerando el impacto de las emisiones de formaldehído.

Esta tesis doctoral se ha dividido en varios capítulos que abordan los principales objetivos del proyecto. En las secciones siguientes se resume brevemente el contenido de cada capítulo, así como las metodologías aplicadas y los principales resultados y conclusiones obtenidos.

Capítulo 1. Introducción: Marco de este trabajo

El capítulo 1 es un capítulo introductorio que contextualiza el marco de esta tesis. En primer lugar, se describe la empresa en la que se llevó a cabo este trabajo. A esto le sigue una explicación del *estado del arte* de los procesos de pintado de vehículos, que es el resultado de una investigación bibliográfica y la visita y evaluación de las plantas de pintura sobre la base de la información proporcionada por ingenieros y operadores de la empresa. Con esta información, se introducen las plantas de pintura de la empresa y se muestran sus particularidades. Por último, se describen el problema de las emisiones de formaldehído que surge en las plantas de pintura de vehículos debido a la mencionada reclasificación y las principales opciones para reducir o eliminar las emisiones de formaldehído.

La empresa Opel cuenta con diez fábricas, seis de las cuales se dedican a la producción de vehículos. El proceso de producción del vehículo se lleva a cabo en diferentes zonas donde se producen, ensamblan y pintan la mayoría de las partes del vehículo. Las cuatro áreas principales involucradas en el proceso de producción son: taller de prensas, taller de carrocerías, taller de pintura y taller de montaje final. En particular, las operaciones de pintado realizadas en el taller o planta de pintura causan los mayores impactos ambientales de todo el proceso de producción. La alta demanda de energía y recursos materiales, el consumo de agua, la generación de residuos y aguas residuales, así como la emisión a la atmósfera de compuestos orgánicos volátiles (COV) son los aspectos ambientales más significativos de los procesos de pintado.

El proceso de pintado de vehículos consiste en una secuencia de procesos de inmersión, así como en la aplicación de pinturas y materiales de recubrimiento utilizando equipos de atomización. Los pasos principales en el proceso de pintado son pretratamiento, cataforesis, sellado de PVC, capa de imprimación, capa de pintura base y capa de laca clara o barniz. Las diversas capas aplicadas en estas etapas garantizan una protección a largo plazo contra la corrosión, las condiciones meteorológicas, la influencia química, etc.

Las distintas capas aplicadas en la carrocería del vehículo se consiguen aplicando recubrimientos y pinturas con diferentes componentes y aditivos que les proporcionan la estabilidad, durabilidad y características visuales necesarias. En general, los componentes básicos de las pinturas son los disolventes orgánicos, el agua, las resinas, los plastificantes, los tintes y los pigmentos. Una de las resinas más usadas en las pinturas de los vehículos son las resinas de melamina, producidas por la reacción de melamina y formaldehído. Por lo tanto, el formaldehído está presente en las pinturas para automóviles como residuo asociado al proceso de fabricación de la resina, pero también como componente ligado a los polímeros de melamina.

Teniendo en cuenta la presencia de formaldehído en las pinturas de los vehículos y su alta volatilidad, caben esperar emisiones de esta sustancia a la atmósfera. En este capítulo se establece la hipótesis sobre las áreas y procesos en los que pueden producirse emisiones de formaldehído. La hipótesis puede resumirse de la siguiente manera:

- En primer lugar, una pequeña cantidad de formaldehído libre presente en las pinturas puede emitirse a la atmósfera a través de los gases residuales procedentes directamente de las cabinas de pintado.

- En segundo lugar, la estructura melamina-formaldehído se rompe durante el proceso de curado de pintura dentro de los hornos de secado a altas temperaturas, liberando formaldehído que se emitirá a la atmósfera si no se instala ningún equipo de reducción de emisiones o si el sistema de reducción no es capaz de eliminar el formaldehído.

Esta hipótesis se analiza a fondo en el capítulo 2.

Las seis plantas de pintura de la empresa fueron consideradas en este trabajo para la evaluación de las emisiones de formaldehído. Se llevó a cabo una evaluación exhaustiva de cada planta como etapa preparatoria para el estudio realizado en el capítulo 2. En el capítulo 1 se indican las diferentes características y condiciones de trabajo de cada planta.

En cuanto a las opciones para reducir o eliminar las emisiones de formaldehído, se hace una distinción entre las emisiones de formaldehído libre de las cabinas de pintado y las emisiones de los hornos de secado. En cuanto a la primera, la purificación de las pinturas para reducir la concentración de formaldehído libre es la medida más adecuada. La opción elegida por los fabricantes de pintura fue mejorar los procesos de fabricación de la resina para eliminar las impurezas del formaldehído. Para eliminar o reducir las emisiones de formaldehído de los hornos de secado, se pueden considerar dos tecnologías alternativas. La primera opción es la instalación de un oxidador térmico regenerativo (RTO en inglés). Este equipo consta de varios lechos con relleno cerámico donde el proceso de oxidación tiene lugar en una serie de pasos alternos de calentamiento y enfriamiento. La segunda alternativa es la oxidación térmica recuperativa, que consiste en una cámara de combustión única en la que se produce la oxidación de los COV. Ambos tipos de tecnología pueden tratar todos los gases residuales de los hornos de secado y se basan en los principios de la oxidación térmica. Las características de cada tecnología se explican en el capítulo 1.

Capítulo 2. Inventario de las emisiones de formaldehído

En el capítulo 2 se describe la primera investigación realizada en las seis plantas de pintura de vehículos de la empresa en relación con las mediciones de las emisiones de formaldehído. En este capítulo se explican la elaboración de los programas de medición y las metodologías aplicadas para las mediciones. Posteriormente, se examinan y exponen los resultados teniendo en cuenta la hipótesis enunciada en el capítulo 1. Se identifican las plantas de pintura y los procesos que requieren medidas correctivas para garantizar el cumplimiento del valor límite de emisión aplicable y se proponen medidas específicas para la reducción de las emisiones de formaldehído. Por último, se muestran los datos de inventario de las emisiones de formaldehído utilizados para el análisis de ciclo de vida (ACV) desarrollado en el capítulo 3.

Para realizar las mediciones de las concentraciones de formaldehído, se elaboraron programas de medición específicos para cada planta de pintura. Se seleccionaron e incluyeron en los programas las chimeneas pertinentes de los procesos afectados. En general, el alcance de las mediciones incluyó los gases residuales de las cabinas de pintado, las zonas de *flash off* y los hornos de secado de los subprocesos de cataforesis, imprimación, capa de pintura base y capa de laca clara. En casos específicos, también se incluyeron los gases residuales procedentes de operaciones menores como el sellado de PVC o la aplicación de ceras. En este capítulo se indican los puntos de medición específicos de cada planta, así como las condiciones de funcionamiento durante el muestreo.

Las mediciones se llevaron a cabo por empresas de medición disponibles en la región donde se encuentra la planta de producción. Estas empresas fueron seleccionadas tras un examen preliminar que aseguró que contaran con la acreditación y los conocimientos necesarios para el muestreo y el análisis de las mediciones de las emisiones de formaldehído. Las empresas aplicaron tres metodologías diferentes (*DNPH Method – Impinger Method, XAD-2 Collection Tubes Method and Multicomponent FTIR Gas Analyzer*), en función de su disponibilidad y acreditación. Estas metodologías se describen en detalle en este capítulo.

Los resultados de las mediciones confirman y validan la hipótesis enunciada en el capítulo 1. Las concentraciones observadas en los gases residuales de las cabinas de pintado en todas las plantas fueron típicamente inferiores a 0.5 mg/m^3 y, por tanto, muy inferiores al valor límite de emisión aplicable. Esto indica que las emisiones de las cabinas no son motivo de preocupación desde el punto de vista legal. Por el contrario, las concentraciones encontradas a la salida de los hornos de secado superan significativamente el valor límite de emisión, con resultados que alcanzan 88.3 mg/m^3. Los resultados también demuestran que las altas concentraciones de formaldehído después del horno pueden reducirse con éxito a valores inferiores al valor límite de emisión aplicable si se instala un equipo de reducción para tratar el gas residual del horno y éste se opera correctamente. Las dos tecnologías consideradas, es decir, la oxidación térmica regenerativa y recuperativa, pudieron reducir el formaldehído obteniendo resultados similares.

Teniendo en cuenta estos resultados, se proponen medidas correctivas para reducir las emisiones de formaldehído en dos plantas en las que se observaron concentraciones elevadas. Estas acciones incluyen el aumento de la temperatura de operación de 540 °C a 730 °C en los sistemas de reducción de emisiones de los hornos de imprimación, la redirección de los gases de la zona de *flash off* de imprimación para ser tratados en dichos sistemas de reducción, la reparación o el reemplazo de piezas dañadas y equipos de reducción antiguos para lograr una eficiencia de destrucción adecuada, y la instalación de equipos de reducción de emisiones en los hornos del proceso de acabado (capa de pintura base y laca clara) cuyos gases residuales se emiten a la atmósfera sin tratamiento.

Como siguiente paso, se llevó a cabo una evaluación de los impactos ambientales y económicos de las diferentes acciones en una de las dos plantas de pintura afectadas. Para ello se realizó un ACV del proceso de pintado en esta planta y un análisis de ecoeficiencia de las diferentes opciones para reducir el formaldehído. Los resultados obtenidos en la planta de pintura estudiada se utilizaron para elaborar el inventario para estos análisis. Ambos estudios se describen en los capítulos 3 y 4.

Capítulo 3. Análisis de Ciclo de Vida

El capítulo 3 se ocupa del ACV del proceso de pintado de vehículos en una planta de pintura en la que se observaron altas emisiones de formaldehído. Esta evaluación se realizó para analizar los impactos ambientales del proceso y comparar estos impactos antes y después de la introducción de las diferentes acciones para reducir las emisiones. Para llevar a cabo este estudio, se definieron diferentes escenarios que se describen en detalle en este capítulo.

Siguiendo la definición de los escenarios, se explican y muestran las metodologías empleadas tanto para el ACV como para la elaboración del Inventario de Ciclo de Vida (ICV) necesario. Por último, se examinan los resultados del análisis, lo que permite comparar los distintos escenarios en relación con su impacto ambiental.

Los escenarios estudiados en el ACV pueden resumirse de la siguiente manera:

- Caso Base: representa la planta de pintura como funcionaba en 2015 antes de que se implementara cualquier acción para reducir las emisiones de formaldehído.

- Escenario A: representa la planta de pintura en 2016 después de que se implementó un primer conjunto de acciones. Éstas consisten en una reducción de la cantidad de formaldehído libre en las pinturas y una disminución de las emisiones del proceso de imprimación mediante la introducción de mejoras técnicas y operativas.
- Escenario B: considera la planta de pintura en el Escenario A con la instalación adicional de un RTO para tratar los gases residuales de los hornos de acabado (2018).
- Escenario C: es una alternativa al escenario B que implica la instalación de varios oxidadores térmicos recuperativos en lugar del RTO para los gases residuales de los hornos de acabado (2018).
- Escenario D: representa la planta de pintura en el Escenario B con la adición de una futura mejora. Esta mejora consiste en un tratamiento completo de las emisiones de las cabinas de aplicación de la capa de pintura base.

Con respecto a la metodología, se realizó un ACV atribucional del proceso de pintado en la planta de pintura estudiada desde una perspectiva “de la cuna a la tumba", siguiendo los requisitos y directrices de las normas ISO 14040:2006 e ISO 14044:2006. Para llevar a cabo el ACV, se realizó un Análisis de Impacto de Ciclo de Vida (AICV) utilizando el software comercial SimaPro v.8.2 con la metodología European ReCiPe Midpoint V1.12, utilizando la base de datos EcoInvent v3.2. Esta metodología tiene en cuenta 18 categorías de impacto.

Para la elaboración del ICV, se recopilaron datos sobre el consumo de materiales y energía, así como datos de residuos y emisiones correspondientes a un año de producción, y se refirieron a la unidad funcional de una hora de funcionamiento. En el presente capítulo se muestran los datos de inventario recopilados para los subprocesos incluidos en el estudio (cataforesis, imprimación, pintura base y laca clara).

Tras la selección de las categorías de impacto y la clasificación de los resultados del inventario, se siguieron los pasos de caracterización y normalización definidos en las normas ISO mencionadas. La caracterización del proceso de pintado en el Caso Base se realizó para identificar el subproceso con mayor impacto ambiental. Además, se realizó la caracterización de cada uno de los subprocesos para reconocer los *inputs* y *outputs* que contribuyen en mayor medida al impacto ambiental. El siguiente paso fue la caracterización del sistema para los Escenarios A, B y C, y finalmente el Escenario D.

A continuación, para facilitar la comparación de los distintos escenarios, se normalizaron los resultados. Para comparar los datos normalizados, se aplicaron dos criterios diferentes en la selección de las categorías de impacto más relevantes:

- Todas las categorías de impacto cuya contribución relativa al impacto medioambiental total fue superior al 2 %.
- Toxicidad humana (HT en inglés) exclusivamente.

Los resultados de la caracterización del proceso de pintado en el Caso Base indican que el proceso de acabado (pintura base y laca clara) causa los mayores impactos ambientales de todo el proceso. Este resultado es razonable debido al mayor consumo de materiales y a la producción de emisiones de este subproceso, al mayor consumo de gas natural y a las emisiones directas sin sistemas de reducción instalados. Además, la cataforesis también se identificó como un proceso con una contribución relevante al impacto ambiental total, principalmente debido a la resina epoxi contenida en la pasta catiónica utilizada en este proceso.

Una vez analizado el proceso completo de pintado, se evaluaron los escenarios de mejora definidos. Los resultados de caracterización del Escenario A se compararon con los del Caso Base. En el proceso de imprimación se observó una disminución del 7 % de la categoría de impacto de toxicidad humana (HT). Por lo tanto, el Escenario A logra reducir la toxicidad humana mediante la reducción de las emisiones de formaldehído. Sin embargo, el mayor consumo de gas natural de este escenario debido al aumento de la temperatura de operación de los equipos de reducción de emisiones condujo a un aumento en casi todas las demás categorías de impacto.

Tras el análisis del Escenario A, se estudiaron los Escenarios B y C. Se observó que ambas tecnologías de reducción evaluadas en estos escenarios lograron una disminución de la toxicidad humana debido a la reducción de las emisiones de formaldehído. Sin embargo, la instalación de oxidadores térmicos recuperativos (Escenario C) alcanzó una reducción de la toxicidad humana más significativa que el RTO (Escenario B). Por otra parte, los oxidadores recuperativos lograron una mejora general al considerar las categorías de impacto más relevantes seleccionadas en este estudio, a diferencia del RTO, que produce un aumento del impacto ambiental. Estos resultados se explicaron por el mayor consumo total de energía de la tecnología de oxidación térmica regenerativa. Por lo tanto, la instalación de los oxidadores térmicos recuperativos es la alternativa más sostenible desde el punto de vista medioambiental.

Por último, se analizó el Escenario D. Este escenario no logró una reducción de la categoría de impacto de HT. La mejora de la HT causada por la reducción de las emisiones de COV y formaldehído de las cabinas de aplicación de la pintura base se compensa con un deterioro debido al aumento del consumo de gas natural.

Los resultados obtenidos en el ACV confirmaron que todos los escenarios estudiados lograron reducir la toxicidad humana si se comparan con la situación inicial de la planta de pintura. Sin embargo, la magnitud de esta reducción es diferente para los diferentes escenarios. La aplicación consecutiva del Escenario A seguida del Escenario C representa la opción más sostenible desde el punto de vista del medioambiente, tanto en vista de la toxicidad humana como del impacto ambiental total.

Capítulo 4. Análisis de Ecoeficiencia de los equipos de reducción de emisiones de formaldehído

El aspecto económico no se ha incluido en la evaluación del capítulo 3. Con el fin de proporcionar a la empresa información adicional para la toma de decisiones y seleccionar la tecnología más adecuada para la reducción de las emisiones de los hornos de acabado, se llevó a cabo una evaluación económica y un análisis de ecoeficiencia. Estas evaluaciones se describen en el capítulo 4. La metodología empleada para el análisis así como la interpretación de los resultados obtenidos figuran en el presente capítulo. En base a estos resultados, se explica y justifica la decisión final de la empresa. En última instancia, en este capítulo se presenta una propuesta para la planta de pintura de vehículos más ecoeficiente considerando el impacto de las emisiones de formaldehído.

La evaluación económica y el análisis de ecoeficiencia se llevaron a cabo para comparar las dos opciones de reducción de las emisiones de los hornos de acabado en la planta de pintura estudiada en el capítulo 3. En la evaluación económica, se recopilaron todos los datos de costes necesarios para realizar el análisis de ecoeficiencia. Estos datos incluyen los costes de instalación, funcionamiento y mantenimiento de los dos sistemas de reducción a lo largo de su vida útil. Los costes totales se normalizaron a la unidad funcional para permitir la comparación entre los dos sistemas. El análisis de ecoeficiencia se realizó sobre la base de los criterios prescritos en la norma ISO 14045:2012.

Para el análisis de ecoeficiencia se utilizaron los resultados de normalización obtenidos previamente en el ACV. Se seleccionaron dos indicadores diferentes, que se compararon con el coste total por hora:

- Variación del índice normalizado, expresada en porcentaje, considerando la suma de las categorías de impacto con una contribución relativa al impacto medioambiental total superior al 2 % en los resultados de la normalización.
- Variación del índice normalizado, expresado en porcentaje, de la categoría de impacto HT.

Los resultados de la evaluación económica figuran en el presente capítulo. Las diferencias significativas en los costes totales de los dos sistemas fueron explicadas. Los resultados del análisis de ecoeficiencia demuestran que, en los casos en que sólo se persigue la reducción de las emisiones de formaldehído para garantizar el cumplimiento legal, junto con una mejora general de la toxicidad humana, y los costes son el principal factor en el proceso de toma de decisiones, el RTO es la opción de reducción de emisiones más favorable desde el punto de vista económico. Los costes totales para la instalación de los oxidadores térmicos recuperativos son 2.2 veces superiores a los del RTO (305.36 €/h y 136.85 €/h, respectivamente). Por lo tanto, la decisión de la empresa de instalar un RTO en los hornos de acabado de la planta de pintura estudiada pudieron justificarse por estos resultados.

Los resultados y conocimientos adquiridos en esta tesis doctoral permiten hacer una propuesta para la planta de pintura de vehículos más ecoeficiente considerando el impacto de las emisiones de formaldehído. Esta propuesta se presenta en el capítulo 4 como resultado principal de este trabajo. En particular, cuando se trata de la reducción de las emisiones de formaldehído de los hornos de acabado, se propuso la instalación de oxidadores térmicos recuperativos como la mejor opción, disminuyendo a su vez la huella ambiental de la planta de pintura.

Conclusiones generales

Esta tesis de doctorado industrial tenía como principales objetivos comprender exhaustivamente las emisiones de formaldehído en las plantas de pintura de las fábricas de producción de vehículos desde una perspectiva medioambiental y legal, proponer y evaluar diferentes posibilidades de reducción o eliminación de estas emisiones y, en última instancia, formular una propuesta para la planta de pintura de vehículos más ecoeficiente considerando el impacto de las emisiones de formaldehído. Los resultados obtenidos en el capítulo 2 en relación con las mediciones de las emisiones de formaldehído en seis plantas de pintura, en el capítulo 3 mediante un Análisis de Ciclo de Vida y, por último, en el capítulo 4 mediante la evaluación económica y el análisis de ecoeficiencia, permitieron alcanzar estos objetivos.

Los resultados de este trabajo proporcionan nueva información a los fabricantes de vehículos y a los operadores de las plantas de pintura, facilitando el proceso de toma de decisiones en la selección de la tecnología de reducción de emisiones de gases residuales más adecuada y otras medidas para la reducción o eliminación de las emisiones de formaldehído.

En este trabajo, se han confirmado el ACV y el análisis de ecoeficiencia como herramientas poderosas que pueden ser aplicadas en el sector industrial durante las actividades de planificación y selección para evaluar e identificar la tecnología más sostenible desde el punto de vista ambiental.

SUMMARY

The classification of substances and mixtures is continuously revised and corrected in the European Union to reflect the adaptions to technical and scientific progress. Thus, the classification of chemicals is regularly updated, and new substances can be reclassified as hazardous. Formaldehyde was reclassified in 2015 as a substance with a higher carcinogenic category, receiving the Hazard Statements H350, *may cause cancer*, and H341, *suspected of causing genetic defects*. Consequently, all industries covered under the Industrial Emissions Directive 2010/75/EU shall, as far as possible, replace formaldehyde with less harmful substances. Moreover, if the emissions of this substance cannot be avoided, a significantly more stringent Emission Limit Value of 2 mg/m^3 in its emission sources must be respected.

One of the industrial sectors affected by the reclassification of formaldehyde is the automotive industry, and in particular the vehicle painting operations due to the presence of melamine resins in the paints´ composition. This change obliged vehicle manufacturers to evaluate their legal situation and implement technical and operational countermeasures to reduce or eliminate formaldehyde emissions.

The project of this industrial Ph.D. thesis is part of the ongoing investigation that the company Opel (hereinafter referred to as “the company”) is conducting to timely recognize and identify the reclassification of chemicals used in its processes and evaluate their environmental and economic impacts. Within this framework, the company needed to assess the impact of the mentioned change in the hazardous classification of formaldehyde on its environmental legal compliance and its economic repercussions. For this purpose, a detailed study was carried out at different vehicle production plants. This study included the evaluation of compliance with the legally applicable emission limit value through measurements of formaldehyde concentrations at the relevant chimneys from the affected painting processes, an evaluation of possibilities to reduce or eliminate the emissions of formaldehyde, comprising raw material substitution and installation of waste gas abatement equipment, and an economic study of the different possibilities. As essential steps of this work, a Life Cycle Assessment (LCA) of the painting process in a real vehicle paint shop and an eco-efficiency analysis of the different alternatives to reduce formaldehyde emissions were conducted. The outcomes and knowledge gathered in this investigation allowed to make a proposal for the most eco-efficient paint shop in view of formaldehyde emissions performance.

This Ph.D. thesis has been divided in several chapters that address the main objectives of the project. The following sections briefly summarize the contents of each chapter as well as the applied methodologies and the main results and conclusions obtained.

Chapter 1. Introduction: Framework of this work

Chapter 1 is an introductory chapter that contextualizes the framework of this thesis. Firstly, the company at which this work was carried out is described. This is followed by an explanation of the current state-of-the-art of the vehicle painting processes, which is the result of bibliographic research and the visit and evaluation of the paint shops based on information provided by company engineers and operators. With this knowledge, the paint shops of study are introduced and their particularities shown. Finally, the formaldehyde emissions problem that arises in the vehicle paint shops due to the mentioned reclassification and the main options to reduce or eliminate the emissions of formaldehyde are described.

The company Opel has ten manufacturing plants, six of them dedicated to the production of vehicles. The vehicle production process is carried out in different areas where most parts of the vehicle are produced, assembled and painted. The four main areas involved in the production process are press shop, body shop, paint shop and general assembly. In particular, the painting operations carried out in the paint shop cause the highest environmental impacts of the whole production process. The high demand of energy and resources, water consumption, the generation of waste and wastewater as well as the emission into the atmosphere of volatile organic compounds (VOCs) are the most significant environmental aspects of the painting processes.

The vehicle painting process consists of a sequence of dipping processes as well as the application of paints and coating materials using atomization equipment. The main steps in the painting process are pre-treatment, electrocoating, PVC sealing, primer coat, basecoat and clearcoat. The several layers applied in these steps guarantee a long-term protection against corrosion, weather conditions, chemical influence, etc.

The layers put in the vehicle body are achieved by applying coatings and paints with different components and additives that provide them with the necessary stability, durability and visual characteristics. In general, organic solvents, water, resins, plasticizers, dyes and pigments are the basic components of paints. One of the most used resins in vehicle coatings are melamine resins, which are produced by the reaction of melamine and formaldehyde. Thus, formaldehyde is present in automotive coatings as a residue associated with the resin manufacturing process but also as a component bound in melamine polymers.

Considering the presence of formaldehyde in vehicle paints and its high volatility, releases of this substance into the atmosphere can be expected. In this chapter, the hypothesis is stated regarding the areas and processes from which emissions of formaldehyde can occur. The hypothesis can be summarized as follows:

- Firstly, a small amount of free formaldehyde present in the paints can be emitted to the atmosphere through the waste gas coming directly from the paint booths.
- Secondly, the melamine-formaldehyde structure is broken during the paint curing process inside the drying ovens at high temperatures, releasing formaldehyde which will be emitted to the atmosphere if no air emissions abatement equipment is installed or if the abatement system is not able to eliminate the formaldehyde.

This hypothesis is analyzed in-depth in chapter 2.

The six paint shops of the company were considered in this work for the evaluation of the formaldehyde emissions. A thorough assessment of each paint shop was conducted as a preparation step for the study carried out in chapter 2. The different characteristics and conditions of the paint shops are shown in chapter 1.

When it comes to the options to reduce or eliminate formaldehyde emissions, a distinction is made between the emissions of free formaldehyde from the paint booths and the emissions from the ovens. Concerning the first, the purification of the paints to reduce the concentration of free formaldehyde is the most suitable countermeasure. An improvement of the manufacturing processes of the resin to eliminate impurities of formaldehyde was the most preferable option selected by the paint manufacturers. To eliminate or reduce formaldehyde emissions from the drying ovens, two alternative technologies can be considered. The first option is the installation of a regenerative thermal oxidizer (RTO). This equipment comprises several beds filled with ceramic medium where the oxidation process takes place in a series of alternative heating and cooling steps. The second alternative is the recuperative thermal oxidation, which consists of a single combustion chamber where the VOCs are oxidized. Both types of technology can treat all waste gases from the ovens and are based on the principles of thermal oxidation. The characteristics of each technology are explained in chapter 1.

Chapter 2. Inventory of formaldehyde emissions

Chapter 2 describes the first main investigation performed at the six vehicle paint shops of the company regarding the formaldehyde emissions measurements. In this chapter, the elaboration of the measurement programs as well as the methodologies applied for the measurements are explained. Subsequently, a discussion of the results is provided in view of the hypothesis stated in chapter 1. The paint shops and processes that need corrective action to ensure compliance with the applicable emission limit value are identified and specific actions for the reduction of the formaldehyde emissions are proposed. Finally, the inventory data of formaldehyde emissions used as input for the Life Cycle Assessment (LCA) developed in chapter 3 is shown.

To carry out the measurements of formaldehyde concentrations, measurement programs were specifically developed for each paint shop. The relevant chimneys of the affected processes were selected and included in the programs. In general, the scope of the measurements included the waste gas from the booths, flash off zones and drying ovens of the electrocoating, primer, basecoat and clearcoat sub-processes. In specific cases, the waste gas from minor operations such as PVC-sealing or waxing were also included. The specific measurement points for each paint shop as well as the operating conditions during the sampling are shown in this chapter.

The measurements were conducted by measuring companies available in the region where the production plant is located. These companies were selected after a preliminary screening ensuring that they had the necessary accreditation and expertise in the sampling and analysis of emissions measurements of formaldehyde. Three different methodologies, i.e. DNPH Method – Impinger Method, XAD-2 Collection Tubes Method and Multicomponent FTIR Gas Analyzer, were applied by the companies depending on their availability and accreditation. These methodologies are described in detail in this chapter.

The results of the measurements confirm and validate the hypothesis stated in chapter 1. The concentrations observed at the waste gas from the spray booths in all paint shops were typically below 0.5 mg/m^3 and thus well below the applicable emission limit value. This indicates that the emissions from the spray booths are not a concern from the legal perspective. On the contrary, the concentrations found at the exit of the drying ovens significantly exceed the emission limit value, with results that reach 88.3 mg/m^3. The results also demonstrate that the high concentrations of formaldehyde after the oven can be successfully reduced to values below the applicable emission limit value if abatement equipment is installed to treat the waste gas from the oven and it is properly operated. The two considered technologies, i.e. regenerative and recuperative thermal oxidizers, were able to reduce formaldehyde achieving similar results.

Considering these results, proposals for actions to reduce the formaldehyde emissions are made for two paint shops where high concentrations were observed. These actions include the increase of the abatement temperature from 540 °C to 730 °C in the primer oven abatement systems, the redirection of the primer flash off waste gas to be treated in these abatement installations, the repair or exchange of damaged parts and old abatement equipment to achieve a proper destruction efficiency, and the installation of abatement equipment at the topcoat ovens whose waste gas was emitted to the atmosphere without treatment.

As a next step, an evaluation of the environmental and economic impacts of the different actions for one of the two affected paint shops was carried out. For this purpose, a LCA of the painting process in this paint shop and an eco-efficiency analysis of the different options to reduce formaldehyde were performed. The measurement results obtained in the paint shop of study were used as input to elaborate the inventory for these assessments. These studies are described in chapters 3 and 4.

Chapter 3. Life Cycle Assessment

Chapter 3 deals with the LCA of the vehicle painting process of one affected paint shop where high formaldehyde emissions were observed. This assessment was performed to analyze the environmental impacts of the process and to compare these impacts before and after the introduction of the different actions to reduce the emissions. To carry out this study, different scenarios were defined. They are described in detail in this chapter.

Following the definition of the scenarios, the methodology applied for the LCA as well as the elaboration of the necessary Life Cycle Inventory (LCI) are explained and shown. Finally, the results of the assessment are discussed, allowing the comparison of the different scenarios in view of their environmental impact.

The scenarios studied in the LCA can be summarized as follows:

- Base Case: it represents the paint shop as it was operating in 2015 before any action was implemented to reduce the formaldehyde emissions.
- Scenario A: it represents the paint shop in 2016 after a first set of actions was implemented. These consist of a reduction of the amount of free formaldehyde in the paints and a decrease of the emissions from the primer process by introducing technical and operational improvements.
- Scenario B: it considers the paint shop in Scenario A with the additional installation of an RTO to treat the waste gas from the topcoat ovens (2018).
- Scenario C: it is an alternative to scenario B which involves the installation of several recuperative thermal oxidizers instead of the RTO for the topcoat ovens waste gas (2018).

- Scenario D: it represents the paint shop in scenario B with the addition of one future improvement. This improvement consists of a complete treatment of the emissions from the basecoat spray booths.

With regard to the methodology, an attributional LCA of the painting process in the paint shop studied was performed from a “cradle-to-grave” perspective following the requirements and guidelines of the ISO 14040:2006 and ISO 14044:2006. To carry out the LCA, a Life Cycle Impact Assessment (LCIA) was conducted using commercial software SimaPro v.8.2 with the European ReCiPe Midpoint V1.12 methodology, using the EcoInvent v3.2 database. This methodology considers 18 impact categories.

For the elaboration of the LCI, material and energy consumption data as well as the waste and emissions data were collected for one year of production and they refer to the functional unit of 1 hour of operation. The inventory data collected for the sub-processes within scope (electrocoating, primer and topcoat) are shown in this chapter.

After the selection of the impact categories and the classification of the inventory results, the characterization and normalization steps defined in the mentioned ISO standards were followed. The characterization of the painting process in the Base Case was performed to identify the sub-process with the greatest environmental impact. In addition, a characterization of each individual sub-process was conducted to obtain the inputs and outputs with the highest contribution to the environmental impact. The next step was the characterization of the system for the Scenarios A, B and C, and finally Scenario D.

As a subsequent step to facilitate the comparison of the different scenarios, the normalization of the results was performed. To compare the normalized data, two different criteria were applied to select the most relevant impact categories:

- All impact categories whose relevant contribution to the total environmental impact was higher than 2 %.
- Human toxicity (HT) exclusively.

The characterization results of the painting process in the Base Case indicate that the topcoat process causes the highest environmental impacts of the whole painting process. This result is reasonable due to the higher consumption of materials and production of emissions of this sub-process, the higher consumption of natural gas, and the direct emissions without installed abatement systems. Moreover, the electrocoating was also identified as a process with a relevant contribution to the total environmental impact, mainly due to the epoxy resin contained in the cationic paste used in this process.

Once the overall painting process was analyzed, the defined improvement scenarios were evaluated. The characterization results of Scenario A were compared to those of the Base Case. A decrease of 7 % of the human toxicity (HT) impact category was observed in the primer process. Therefore, Scenario A achieves the pursued reduction of the human toxicity through the formaldehyde emissions reduction. However, the higher natural gas consumption of this scenario due to the increase of the abatement temperature led to an increase in almost all other impact categories.

Following the analysis of Scenario A, Scenarios B and C were studied. It was observed that both abatement technologies evaluated in these scenarios achieved a decrease in the human toxicity due to the reduction of formaldehyde emissions. However, the implementation of recuperative thermal oxidizers (Scenario C) reached a more significant human toxicity reduction than the RTO (Scenario B). On the other hand, the recuperative oxidizers achieved an overall improvement when considering the most relevant impact categories selected in this study, unlike the RTO, which yields an increase of the environmental impact. These results were explained by the higher overall energy consumption of the regenerative thermal oxidation technology. Thus, the installation of the recuperative thermal oxidizers is the most environmentally sustainable alternative.

Finally, Scenario D was analyzed. This scenario did not achieve a reduction of the HT impact category. The improvement in the HT caused by the reduction of VOC and formaldehyde emissions from the basecoat spray booths is compensated by a deterioration due to the increase of the natural gas consumption.

The results obtained in the LCA confirmed that all studied scenarios achieve the pursued reduction of the human toxicity if they are compared to the original situation of the paint shop. However, the magnitude of this reduction is different for the different scenarios. The subsequent implementation of Scenario A followed by Scenario C represents the most environmentally sustainable option in view of both human toxicity and the total environmental impact.

Chapter 4. Eco-efficiency analysis of abatement equipment for formaldehyde emissions reduction

The economic aspect has not been included in the evaluation of chapter 3. In order to provide the company with additional input for the decision-making and select the most suitable technology for the abatement of the topcoat oven emissions, an economic evaluation and an eco-efficiency analysis were conducted. These assessments are described in chapter 4. The methodology used for the analysis as well as a discussion of the results is provided in this chapter. Furthermore, the final decision of the company considering all the results obtained in this work is explained and justified. Ultimately, in this chapter a proposal for the best eco-efficient paint shop in view of formaldehyde emissions performance is given.

The economic evaluation and eco-efficiency analysis were performed to compare the two abatement options for the topcoat ovens emissions of the paint shop studied in chapter 3. For the economic evaluation, all cost data necessary to carry out the eco-efficiency analysis were collected. These data include installation, operational and maintenance costs of the two abatement systems over their lifetime. The total costs were normalized to the functional unit to allow the comparison between the two systems. The eco-efficiency analysis was conducted based on the criteria prescribed in the ISO 14045:2012.

For the eco-efficiency analysis, the normalization results previously obtained in the LCA were used. Two different indicators were selected and represented against the total cost per hour:

- Variation of the normalized index, expressed in percentage, considering the sum of the impact categories with a relevant contribution to the total environmental impact greater than 2 % in the normalization results.
- Variation of the normalized index, expressed in percentage, of the HT impact category.

The results of the economic assessment are shown in this chapter. Significant differences in the total costs of the two systems were observed and explained. The results of the eco-efficiency analysis demonstrate that in cases where only the reduction of the formaldehyde emissions to ensure legal compliance along with an overall improvement of the human toxicity are pursued and the costs are the main factor in the decision-making process, the RTO is the most economically favorable abatement option. The total costs for the implementation of the recuperative thermal oxidizers were 2.2 times those of the RTO (305.36 €/h and 136.85 €/h, respectively). Thus, the decision of the company to install an RTO at the topcoat ovens of the studied paint shop could be justified by these results.

The results and knowledge acquired in this Ph.D. thesis allow to make a proposal for the best eco-efficient paint shop in view of formaldehyde emissions performance. This proposal is made in chapter 4 as the main outcome of this work. In particular, when it comes to the reduction of the formaldehyde emissions from the topcoat ovens, the installation of recuperative thermal oxidizers was proposed as the best option to reduce the emissions decreasing the environmental footprint of the paint shop.

General Conclusions

This industrial Ph.D. thesis had the main objectives to gain a deep understanding of the formaldehyde emissions in paint shops of vehicle manufacturing plants from both an environmental and a legal compliance perspective, to propose and evaluate different possibilities for the reduction or elimination of these emissions, and ultimately, to formulate a proposal for the best eco-efficient paint shop in view of formaldehyde emissions performance. The results obtained in chapter 2 regarding the formaldehyde emissions measurements at six vehicle paint shops, in chapter 3 by means of a Life Cycle Assessment, and finally in chapter 4 through the economic evaluation and the eco-efficiency analysis, made possible to achieve these objectives.

The outcomes of this work provide new information to vehicle manufacturers and paint shop operators, facilitating the decision-making process in the selection of the most suitable abatement technology and further actions for the reduction of formaldehyde emissions.

LCA and eco-efficiency analysis have been confirmed as powerful tools that can be applied during the planning and selection activities to evaluate and identify the most environmentally sustainable technology.

OBJECTIVES AND MOTIVATION OF THIS WORK

The project of this industrial Ph.D. thesis is part of the ongoing investigation that the company Opel (hereinafter referred to as “the company”) is conducting to timely recognize and identify the reclassification of chemicals used in its processes, in particular in processes associated with painting operations in vehicle assembly plants, and evaluate the environmental and economic impact of such reclassifications.

With one of the latest legal changes with regard to classification of hazardous substances, formaldehyde was reclassified to receive the hazard statements H350, may cause cancer, and H341, suspected of causing genetic defects. With this higher cancer-causing classification, the obligations on the substitution of hazardous substances and control of emissions established by European legislation are immediately applicable. The company needs to evaluate the impact of the mentioned reclassification of formaldehyde on its environmental legal compliance and the economic repercussions.

A detailed study is required at different vehicle production plants to assess the impact of the reclassification. This study includes the evaluation of compliance with air emission limit values through measurements of formaldehyde concentrations at the relevant chimneys from the affected painting processes, an evaluation of possibilities to reduce or eliminate the emissions of formaldehyde including raw material substitution and installation of waste gas cleaning devices, and an economic study of the different possibilities. As an essential part of this work, a Life Cycle Assessment (LCA) of the painting process in a real vehicle paint shop and an eco-efficiency analysis of different options to reduce formaldehyde emissions were carried out in order to define the most eco-efficient paint shop in view of formaldehyde emissions performance.

This industrial Ph.D. thesis has been divided in several stages aiming to address the main objectives of the project. The main objectives can be summarized as follows:

- Evaluation of the state-of-the-art technologies for the vehicle painting processes and environmental control equipment supported by bibliographic research.
- Understanding the formaldehyde emissions in vehicle paint shops from both an environmental and a legal compliance perspective.

- Evaluation of the different possibilities to reduce or eliminate the emissions of formaldehyde.
- Economic assessment of the control equipment for formaldehyde emissions reduction.
- Life Cycle Assessment (LCA) and eco-efficiency analysis to determine the most sustainable option to reduce formaldehyde emissions.
- Formulate a proposal for the best eco-efficient paint shop in view of formaldehyde emission performance.

In chapter 1, the framework of this work is presented, including the description of the company, the production plants and the paint shops of study. Moreover, an explanation of the current vehicle painting processes is given as a result of the bibliographic research and the visit and evaluation of the paint shops based on information provided by paint shop engineers and operators. Finally, a detailed description of the formaldehyde emissions problem as well as an explanation of the main options to reduce or eliminate the emissions of formaldehyde is given.

In chapter 2, the first main investigation conducted in the paint shops of study is carried out. Measurements of formaldehyde emissions were performed at six paint shops to evaluate the main sources of formaldehyde and the legal compliance situation with and without VOC emissions control equipment, and to propose possible corrective actions in emission sources with high concentrations of formaldehyde.

In chapter 3, the Life Cycle Assessment (LCA) is performed to analyze the environmental impacts of one of the six paint shops before and after the introduction of different countermeasures to reduce formaldehyde emissions. For the collection of inventory data, real data from the paint shop of study was used, including the results of the formaldehyde measurements carried out previously, as shown in chapter 2.

Chapter 4 deals with the economic and eco-efficiency analysis of the two different control equipment technologies studied for the reduction of the formaldehyde emissions. Real monetary data from equipment manufacturers and paint shop engineers and operators were used to carry out this evaluation. Ultimately, a proposal is made for the best eco-efficient paint shop considering the reduction of formaldehyde emissions as a priority, taking into account the results of the eco-efficiency analysis as well as the Life Cycle Assessment.

1 INTRODUCTION: FRAMEWORK OF THIS WORK

Vehicle manufacturing is one of the most complex industrial manufacturing processes because it requires large spaces as well as the sequential and coordinated operation of multiple technologies (Bysko et al., 2020; Giampieri et al., 2022). Painting operations have been identified as the stages with the greatest environmental impacts of the entire production process (VDI guideline 3455:2013-08; Onofre et al., 2020). The high demand for energy and resources, such as natural gas and raw materials for the production of coatings and paints, water consumption along with the generation of waste and wastewater are the most significant environmental aspects associated with the painting operations of vehicle assembly plants (STS BREF, 2020). In particular, when it comes to identifying the most polluting compounds in this type of facility, the environmental impact is marked by the emission of volatile organic compounds (VOCs), which represent the most relevant direct emissions. They are derived from spray booths, drying ovens and cleaning of equipment with organic solvents (Rivera and Reyes-Carrillo, 2014; Rivera and Reyes-Carrillo, 2016; Ou et al., 2022). The European Union (EU) car manufacturers emitted in 2021 an average of 2.2 kg/car and a total of 25.7 thousand tons of VOCs due to their vehicle painting activities (ACEA, 2022), which corresponds to 2.5 % of the total VOCs emitted in Europe (German Environment Agency, 2023).

An exhaustive analysis of the paints and coatings used in a vehicle painting plant allows the identification of complex mixtures formulated from numerous components (Akafuah et al., 2016). In general, organic solvents, water, resins, plasticizers, dyes and pigments are the basic components of paints, being the binder (i.e. the resins) the predominant constituent defining the paint´s characteristics (McMahon et al., 2023). Additionally, new developments in automotive paints include the use of nanoparticles as fillers (Nayane de Queiroz et al., 2022). The solvent content of color basecoats is in the range of 12-17 % in water-based and 55-82 % in solvent-based paints, while clearcoats typically have a solvent content up to 50 % (STS BREF, 2020). One of the most commonly used binding agents in industrial coatings are amino resins and, mainly, those derived from melamine (Pizzi and Ibeh, 2022). Melamine resins used in automotive coatings are produced by the reaction of melamine and formaldehyde (Poth, 2008).

This chapter partially reproduces content already published as “Granadero, D. [a b], Garcia-Muñoz, A. [b], Adam, R. [b], Omil, F. [a] and Feijoo, G. [a], 2023. Evaluation of abatement options to reduce formaldehyde emissions in vehicle assembly paint shops using the Life Cycle methodology. Cleaner Environmental Systems, 11, 100139. ISSN 2666-7894, https://doi.org/10.1016/j.cesys.2023.100139.

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Paint manufacturers indicate melamine resin contents varying from 0.1 % to 18 %, depending on the type of coating. Other amino resins used in coatings, such as those derived from urea or (meth)acrylamide, are also obtained by the reaction of different chemicals with formaldehyde (Pizzi and Ibeh, 2022). Thus, formaldehyde is present in automotive coatings as a residue associated with the resin manufacturing process (with a concentration below 0.1 %, as indicated in Safety Datasheets) but also as a component bound in melamine polymers.

Concerning the identification of formaldehyde sources, the emission of small quantities of this compound into the atmosphere present in the exhaust gas flow of the spray booth has been quantified at very low levels (Kim et al., 2011). However, also the bound formaldehyde from melamine resins is released from inside the drying chambers, which operate at elevated temperatures (Salthammer et al., 2010; Salthammer, 2019); therefore, depending on the configuration of the coating line and the efficiency of the end-of-process abatement equipment connected to the drying ovens, the formaldehyde emission can be significant (Sorrels et al., 2017). At present, not all vehicle painting facilities located in Europe have abatement equipment installed in the drying ovens (STS BREF, 2020). This depends on the specific legal requirements of each country, their specific set-up and the subsequent retrofitting steps from the plant assembly to the present time. Besides, the use of abatement equipment can be related to the type of paints used in the paint shop. For instance, in 2016, 43 % of the EU paint shops were estimated to apply solvent-based primer or basecoats, or a combination of both. This type of paint shops are more likely to have air emissions abatement equipment (STS BREF, 2020).

In 2015, formaldehyde was reclassified as a substance with carcinogenic potential (category 1B) and mutagenic potential (category 2) in the amendments to the so-called CLP Regulation on classification, labelling and packaging of substances and mixtures (Regulation (EC) No 1272/2008; Regulation (EU) No 605/2014; Regulation (EU) No 2015/491). With this change, all EU industries affected by the Industrial Emissions Directive 2010/75/EU shall, as far as possible, replace formaldehyde with less harmful substances. If formaldehyde emissions cannot be avoided, what is the case for painting operations in the automotive industry due to the use of the melamine resins, operators need to cope with significantly more stringent Emission Limit Values (Directive 2010/75/EU).

Different technologies are available for the removal of VOCs from exhaust gases. These include biological treatment, recuperative thermal oxidation, regenerative thermal oxidation and catalytic oxidation (Mulholland and Dyer, 1999; Berenjian et al., 2012; Tomatis et al., 2019; Li et al., 2023). In the automotive industry, for the treatment of VOCs in vehicle paint shops, regenerative thermal oxidation and recuperative thermal oxidation, the latter sometimes in combination with catalytic oxidation, have been commonly applied (VDI guideline 3455:2013 08; STS BREF, 2020). Recuperative thermal oxidizers consist of a single combustion chamber where the VOCs are oxidized. On the other hand, regenerative thermal oxidizers comprise several beds filled with ceramic medium where the oxidation process takes place in a series of alternative heating and cooling steps. Both technologies have proven to be efficient in VOC destruction with efficiencies higher than 95 % (STS BREF, 2020). The introduction of catalytic oxidation to recuperative oxidizers allowed the reduction of the high operating temperatures from 700 °C–740 °C to 400 °C necessary to obtain the desired abatement efficiency, with the consequent reduction in natural gas consumption (Yang et al., 2019; STS BREF, 2020; Brummer et al., 2022). However, this technique is not in use in vehicle paint shops because of the high maintenance requirements of the catalyst (STS BREF, 2020).

Given that both regenerative and recuperative thermal oxidation present important differences, the selection between one of them will depend on various aspects such as the VOC levels in the inlet gas, the flowrates to be treated, the spaces available in the paint shop, and the investment restrictions of the paint shop operator (Borwankar et al., 2012). In the selection of the most suitable technology, it is also crucial to consider the environmental impact of both technologies from a life cycle perspective in order to search for the most sustainable treatment method and take it into account in the decision-making process (Klöpffer and Grahl, 2014).

Due to the mentioned European reclassification of formaldehyde, the company carried out an exhaustive investigation in all its paint shops, which is the basis for the development and writing of this Ph.D. thesis. Measurements of formaldehyde emissions were performed at the most relevant areas of the paint shop in order to identify whether the emission limit values established by the applicable European legislation (Directive 2010/75/EU) were met. As a result of these measurements, several areas were identified in one of the painting facilities with high levels of formaldehyde and proposals to reduce the emissions were made. These proposals include discussions with paint manufacturers to reduce or eliminate the sources of formaldehyde in the formulation of paints and other coating materials, modifications in operating conditions of the painting processes and the installation of air emissions abatement equipment. Furthermore, a “cradle-to-grave” LCA study was carried out in order to analyze and compare the environmental impact of the different improvement actions implemented or considered to reduce the formaldehyde emissions at this painting facility. As an essential step after the LCA, an eco-efficiency analysis of two proposed scenarios corresponding to two different abatement technologies was also performed. The relevant cost data needed were obtained by an economic evaluation of the two abatement systems. This type of analysis is not available in the literature and it aims at demonstrating that the LCA methodology and eco-efficiency analysis can be used by vehicle manufacturing companies and paint shop operators to evaluate different process alternatives and favor the most environmentally sustainable technologies. Finally, the outcomes of the LCA and eco-efficiency analysis were used to define the most eco-efficient paint shop in view of formaldehyde emissions performance.

1.1 THE COMPANY

Opel is a German vehicle manufacturer and one of the most important European companies in the vehicle industry. Its central headquarters are located in Rüsselsheim, Hesse, Germany, where the main activities of this work have been carried out.

The history of this company begins in 1862 when Adam Opel opened a sewing machine factory in Rüsselsheim. The company was growing along the years with different products as sewing machines, bicycles, motorbikes and finally, in 1899 the first passenger vehicle was produced.

Opel and its British sister, Vauxhall, are present in over 50 countries, selling nearly one million vehicles per year. From 1929 to 2017, Opel was a subsidiary company of the American group General Motors. In 2017, Opel was transferred to the PSA group. In 2021, the Stellantis group was formed by the merge between the PSA group and the FCA group, building one of the biggest vehicle manufacturers worldwide.

The company has 10 manufacturing plants, six dedicated to vehicle production, as shown in Figure 1, and four to powertrain and components manufacturing along Europe, as well as four development and test centers. Those plants along with central offices give employment to more than 25.000 people (*Internal Information*).

Figure 1. Location of Opel/Vauxhall vehicle manufacturing plants.

1.2 THE VEHICLE PAINTING PROCESS

Vehicle production is one of the major manufacturing industries in Europe. The whole process is carried out in different areas where most parts of the vehicle are produced, assembled and painted to obtain high quality products that meet the customer needs and requirements. The engines and other parts of the vehicle are usually manufactured in other plants with different manufacturing processes.

Figure 2 shows a simplified scheme with the main stages involved in current vehicle manufacturing processes. The inputs to the production plant are energy, with electricity and natural gas as the main sources, raw materials and components necessary for the vehicle production, and water to run the installations and cleaning, principally used in the paint shop processes. The main environmental aspects associated to the production process are air and water emissions, as well as the generation of waste.

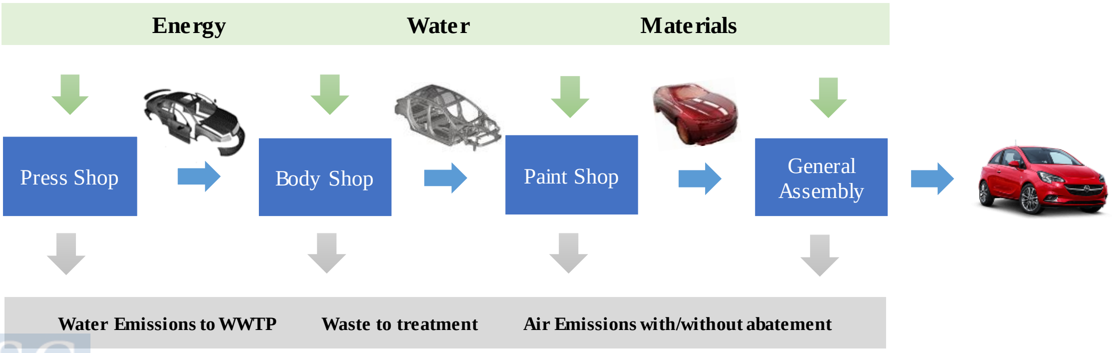

Figure 2. Simplified scheme of the main inputs and outputs in vehicle manufacturing processes.

Vehicle manufacturing processes can thus be divided in four important areas:

- **Press shop**: In the press shop, the stamping and metal forming processes take place to give the vehicle shell the required shape and geometry. The main raw material in these processes is a coil of aluminum or steel which is taken to a stamping line with different mechanical or hydraulic presses to form the vehicle panels. In this stage, there is a matrix cleaning process where a high amount of oily wastewater is generated. Usually, this wastewater stream is treated in a separated wastewater treatment plant (WWTP) (Omar, 2011; Integrated Environmental Authorization, 2014).
- **Body shop**: The body shop comprises all activities related to the joining the vehicle panels by means of welding machines and robots to provide shape and dimensions to the vehicle's shell. The resultant product is called body in white (BiW), which is the bodywork completely joined, ready to be painted (Omar, 2011). The main environmental aspect in this stage is the usage of electricity.
- **Paint shop**: The paint shop is the area where the vehicle coating and painting activities take place. The BiW coming from the body shop undergoes a sequence of dipping processes as well as the application of paints and coating materials using atomization equipment (Streitberger and Dössel, 2008). The different layers applied provide chemical and corrosion protection, weather and scratch resistance, as well as color and visual characteristics (Akafuah et al., 2016). The paint shop is the area with the highest water and energy consumption as well as the generation of waste, wastewater and emissions to air (VDI guideline 3455:2013-08; Onofre et al., 2020, STS BREF, 2020). The main focus of this work is given to the painting process and thus a detailed explanation of this process can be seen in the next section.
- **General assembly**: This is the final area of the vehicle manufacturing process where all the parts and components of the car, usually more than 300 interior and exterior components, are installed and connected to obtain the final product. In this process, wastewater with rests of organic solvents is produced and subsequently treated with a physical-chemical treatment in the WWTP (Omar, 2011; Integrated Environmental Authorization, 2014).

1.2.1 Painting steps

The vehicles are painted not only to obtain the desired appearance, but also a long-term protection against corrosion, weather conditions, chemical influence (e.g. bird droppings, acid rain), chipping, sun, abrasion in car washes, etc. must be guaranteed. This can only be achieved by application of several layers designed to complement each other. To ensure the efficiency of the process, these layers of paint must be applied and dried quickly by using different technologies and equipment (STS BREF, 2020). Figure 3 shows a scheme of the commonly applied painting process. Depending on the age and characteristics of the painting plant, the product, and other specific quality requirements, the painting steps could vary from those in the picture.

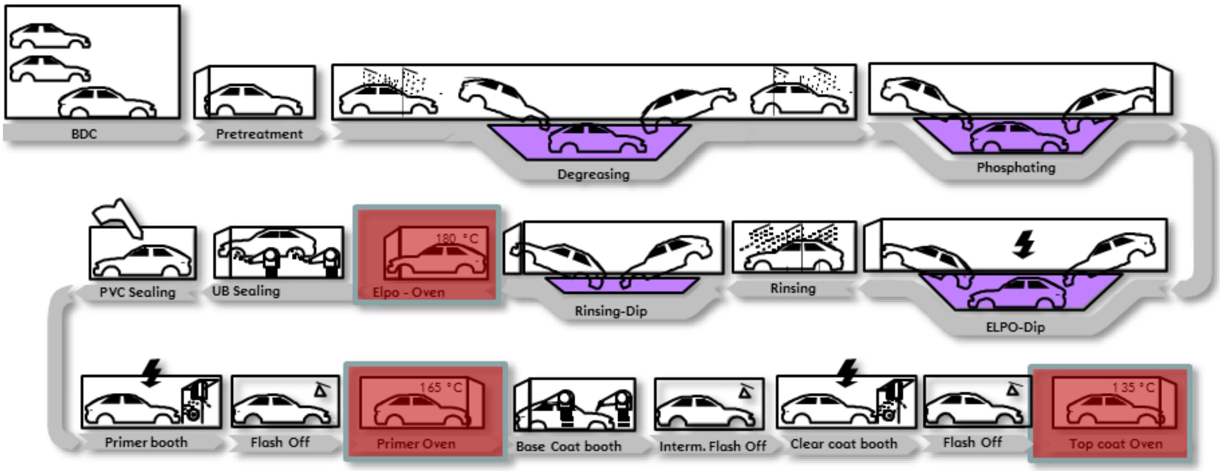

Figure 3. Example of the main painting processes in a vehicle manufacturing painting plant.

The main steps in the vehicle painting process are pre-treatment, electrocoating, PVC sealing, primer coat and topcoat. The latter is a combination of the basecoat and clearcoat.

Pre-treatment

Before the main coating layers are applied to the vehicle body, a series of pre-treatment stages are carried out to clean and condition the body for the next painting steps (Debnath, 2013).

The first stage is the pre-cleaning, followed by two or three degreasing phases. These steps remove oil, grease and lubricants from the previous manufacturing processes. After cleaning, an activation, a phosphating, a passivation and, finally, various rinsing and drainage stages are applied to increase the corrosion resistance of the vehicle body and prepare it for the next coating processes (Giampieri et al., 2020).

The wastewater and sludge generated in these processes are removed constantly by filtration techniques and the treated water is typically reused in the same process (Streitberger and Dössel, 2008; Omar, 2011; VDI guideline 3455:2013-08).

Electrocoating

After the pre-treatment, the first main coating process is the electrocoating, in which the vehicle body is coated in a bath by applying the cataphoretic paint, providing additional corrosion resistance (Giampieri et al., 2020). In this electrochemical process, the paint is deposited on the metal by passing electric current through the body, causing paint to deposit on the surface in a uniform protection layer throughout the whole body (Marder and Goodwin, 2023). The electrocoating paint consists of an aqueous solution made of resins, pigments, additives and solvents. The metal surface acts as the cathode and the paint particles as the anode.

As in all other processes, this step is continuously monitored to ensure a good performance. The most important control factors are: voltage and current density to create the electromagnetic field, bath temperature, pH, paint conductivity, amount of solids, and electrolyte concentration.

After the electrocoating bath, a rinsing process is carried out with the same aqueous solution mixed with water to remove all paint particles that have not been electrically deposited in the metal surface but could still remain on the vehicle body. To reduce paint losses, the multiple rinsing systems use ultrafiltration to regenerate solids and liquids. The rinsing solution highly loaded with solids is then recirculated to the immersion bath reducing the amount of paint required and obtaining a closed loop.

Following the electrocoating, a first drying oven is placed to dry and cure the applied paint films. The high temperatures needed to dry the paint cause the release of VOC. Usually, an air emissions abatement installation is in place to treat the waste gas streams, and thus eliminate VOC. As a consequence of the oxidation process, NOx and CO are released to the atmosphere.

The wastewater from the phosphating and electrocoating processes is treated before the WWTP. The treatment consists of pH adjustment followed of a neutralization to stabilize the wastewater (Streitberger and Dössel, 2008; Omar, 2011; VDI guideline 3455:2013-08; STS BREF, 2020).

Under body sealing, PVC

Once the electrocoating has been completed, additional coating processes are applied for waterproof sealing of body and weld seams and to protect the underbody from damage with an elastic top layer.

The underbody sealant with polyvinylchloride (PVC) materials are applied in areas with a higher corrosion potential such as joints and seams. Depending on the installation, this step can be carried out by hand or robotic application systems, although a combination of both procedures is usually used (Streitberger and Dössel, 2008; Omar, 2011; VDI guideline 3455:2013-08; STS BREF, 2020).

Primer coat

After sealing and underbody coating, the primer coat or primer surfacer is applied in a spray booth where this first paint layer is typically sprayed by robots. The primer application is conducted to solve the possible slopes from the previous coating, prepare the surface for the next paint coat application, achieve adhesion stability by building a layer with the required thickness and quality and ensure a stone chip and UV radiation protection.

Inside the spray booth there is a constant air flow in descendent direction to remove the overspray and avoid the formation of bubbles or excesses.

After the spray application, there is a flash off area followed by a drying oven to evaporate the solvents and cure the primer coating. In both the flash off area and oven the release of VOCs occurs, which are usually treated by an installed abatement system. Consequently, NOx and CO from the oxidation process are emitted (Streitberger and Dössel, 2008; Omar, 2011; VDI guideline 3455:2013-08; STS BREF, 2020).

Topcoat (Basecoat + Clearcoat)

The successive application of the basecoat (BC) and the clearcoat (CC) is commonly referred to as the topcoat. While the primer provides the vehicle body with further corrosion resistance and protection against stone chip, the basecoat and the clearcoat are mainly applied to add the required color and gloss effects to the vehicle. Moreover, the basecoat and the clearcoat give durability and protection against scratches and chemical aggressions (Jurgetz, 1995).

Similar to the primer process, the basecoat and clearcoat are applied in spray booths. Nowadays, most paint shops are equipped with robots that carry out the basecoat and clearcoat application. In some cases, the topcoat process is still conducted manually, especially for interior painting.

Regarding the basecoat, a high number of paints and paint types, including a variety of colors, are available for vehicle manufacturers. Usually, during the painting process the viscosity of the paint must be adjusted by adding water or solvent depending on its composition. In each color change, automatic cleaning with purge solvents is carried out inside the application guns and robots to ensure that the rests of the previous color are completely eliminated. This activity generates a significant amount of solvent waste. Typically, the vehicle manufacturing plants send this solvent waste to an external company to be recycled.

The clearcoat is applied to protect the color pigments from the environment, scratches and chemical aggressions. Moreover, the clearcoat provides the gloss effects to the vehicle. It is applied above the basecoat when this is not completely dry. Usually, a small flash off area is available between the basecoat and the clearcoat to remove water and solvents from the basecoat layer (Streitberger and Dössel, 2008; Omar, 2011; VDI guideline 3455:2013-08; STS BREF, 2020).

The complete drying step for both coating layers takes place in a drying oven placed at the end of the topcoat process. The oven is usually operated at around 150 °C. As described for the primer process, VOCs are released from both the flash off area and the oven. In most cases, the VOCs are treated in an installed abatement system causing NOx and CO emissions.

Beneath the painting booths in primer, basecoat and clearcoat processes, water scrubbers are installed to collect the overspray and remaining paint rests. The wastewater generated in this area is taken to a wastewater tank that contains coagulants in order to separate the water from the paints. In this way, the water can be recirculated and used in the same water scrubber system and the paint sludge can be collected for its disposal.

After the topcoat process, additional waxing, sealing and repairing operations on the dried topcoat complete the process and ensure that the desirable quality and corrosion protection requirements are met (Giampieri et al., 2020).

1.2.2 Paints and their constituents

The several stages of the vehicle painting process apply different coating layers to the vehicle body. These layers have different thicknesses that are necessary to achieve the quality and protection requirements for the vehicle. The next figure shows the different painting layers in a vehicle and their required thickness.

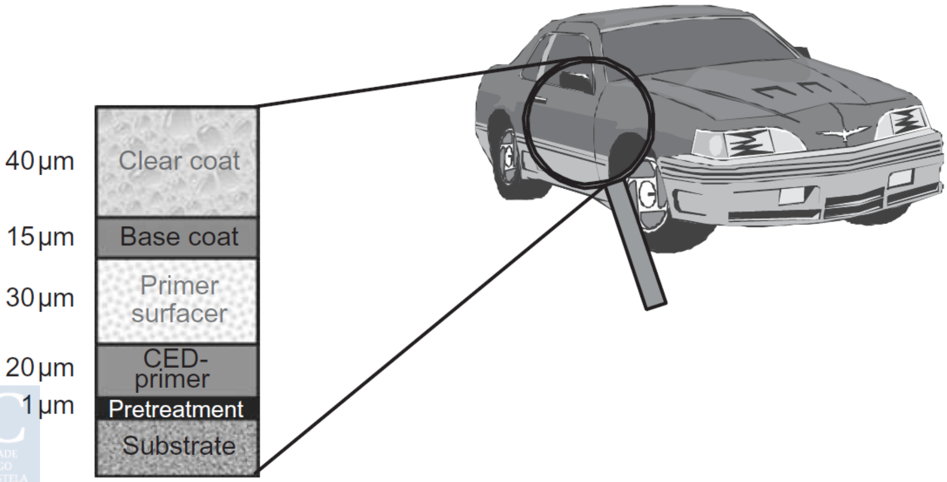

Figure 4. Multilayer coating of cars (Streitberger and Dössel, 2008).

These layers are achieved by applying coatings and paints with a set of components and additives that provide them with the necessary stability, durability and visual characteristics. The main components of paints are (Stoye, 1993; Stoye and Freitag, 1998; Wicks et al., 2007; McMahon et al., 2023):

- **Binders or resins**: The binder (i.e. resins) is the predominant constituent defining the paint´s characteristics. Binders provide adherence and resistance against mechanical and chemical strain. Amino resins derived from melamine are the most used resins in the automotive industry. These resins are made by the reaction of melamine, and formaldehyde (Poth, 2008).
- **Pigments**: They provide color, opacity and usually improve the resistance against corrosion. The clearcoat paint is the only paint without pigment.
- **Additives**: They improve aspect, biological properties, conservation, etc., protects against transport, and prevent defects in the coating such as bubbles, poor levelling or flocculation. Different additives are used depending on the requirements of the paints.
- **Fluidizing medium**. Depending on the chosen fluidizing medium the paints can be waterborne or solvent borne. Additionally, a different kind of paints based on a powder system is also available, however this system is typically not applied in European paint shops. All paints contain different quantities of solvents in their composition.

1.3 THE PAINT SHOPS OF STUDY

All paint shops of the company´s six vehicle manufacturing plants were considered for the evaluation of the formaldehyde emissions in the framework of this study. In order to develop the measurement program, a comprehensive study was necessary to identify and understand the particularities of each paint shop. While the painting steps are the same for the six paint shops and follow the sequence explained in this chapter, each paint shop has different conditions which need to be considered. Two paint shops use solvent-based basecoat paints and four use waterborne basecoat paints; four paint shops collect almost all their waste gas streams from the spray booths and discharge them through one chimney to the atmosphere, whereas the other two paint shops have individual chimneys for each sub-process or painting booth. Another significant difference can be observed in their VOC emissions control technology implemented. Table 1 shows a summary of the main conditions identified in the six paint shops, which was elaborated from a data collection exercise consisting of information provided by paint shop operators.

Table 1. Collection of paint shop conditions – survey data.

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Whereas:

Product:

- PC: Passenger car
- LCV: Light Commercial Vehicle

SOP: Start of production

Subst. Change: Last substantial change carried out in the paint shop, e.g. change in technology from solvent based basecoat to waterborne basecoat, installation of new VOC abatement equipment, retrofit of painting application devices: automatization.

PT-EC: Pretreatment and Electrocoating

SD: Sealing and dumping

PR: Primer application

TC: Topcoat application (Basecoat + Clearcoat)

Other: Additional lines, e.g. special vehicles, repair lines

JPH: Job per hour, number of vehicles painted in one hour of production

PT: Pretreatment

EC: Electrocoating

BC: Basecoat

CC: Clearcoat

CP: Cavity preservation (wax)

PHO: Phosphating

SB'1k: Solvent based one-component

WB: Water based coating

SB: Solvent based coating

Recup.: Recuperative Thermal Oxidizer

RTO: Regenerative Thermal Oxidizer

All the information summarized in Table 1 constitute the basis for the elaboration of the measurement programs for formaldehyde emissions as described in chapter 2.

1.4 THE FORMALDEHYDE EMISSIONS PROBLEM

Formaldehyde (Verbände-Positionspapier, 2014) is a simple organic volatile compound with the chemical formula H-CHO. Formaldehyde is a colorless gaseous substance that has a typical pungent odor that can be perceived even at very low concentrations. All organic life forms produce formaldehyde that is emitted to the environment. In the human body, formaldehyde is synthesized as part of natural metabolism, a portion of which is exhaled in the air we breathe (0.001 to 0.01 mg/m3). Large amounts of formaldehyde are also emitted by forests, for example. It is formed during the photochemical decomposition of organic substances in the air and during all incomplete combustion processes.

Formaldehyde has a wide range of industrial applications. It is produced synthetically on a large scale and is widely used as intermediate and end product. At the time this work was started, around 21 million metric tons were produced worldwide each year. This germicidal, preservative and disinfectant substance is contained in numerous everyday products, for example in disinfectants, household cleaners, cosmetics, various paints and varnishes, and in building products. Many industries, such as the automotive industry, chemical industry, ceramic industry, foundries, plaster industry, wood industry, paint manufacturing industry and textile industry, either directly utilize formaldehyde in their production or supporting processes or formaldehyde emissions occur due to decomposition or incomplete combustion processes (ACEA, 2014; Formacare, 2014; Verbände-Positionspapier, 2014).

In the automotive industry, formaldehyde has many different applications which vary from the use of formaldehyde-based resins in fuel pumps, transmission parts and brake pads, to other applications such as decorative laminates of car interiors, engine lubricants, vulcanized rubber tyres and lightweight polyurethane foams for automobile door insulation (Formacare, 2014). In the last years, almost 9 % of the total formaldehyde production in Europe was melamine formaldehyde resins. These resins are fast-curing and can resist high temperatures and chemical damages so that they are usually used in the composition of surface coatings of vehicles (Formacare, 2014; Roth and Rupp, 2014; Bolt et al., 2016). In the vehicle manufacturing plants, the problem with formaldehyde emissions arises in the paint shops due to the use of melamine formaldehyde resins in the paints.

1.4.1 Formaldehyde in vehicle paints

As explained above, the binder is one of the essential constituents of the paints used in vehicle painting. The most extended binders are melamine formaldehyde resins due to its chemical properties (Formacare, 2014; Roth and Rupp, 2014; Bolt et al., 2016; Pizzi and Ibeh, 2022) that guarantee UV resistance and shock resistance. In the melamine formaldehyde resins, formaldehyde is part of the polymer, in which it forms chemical bonds with melamine (Figure 5). It functions as a chemical protective group which ensures that no unwanted chemical reaction between melamine molecules takes place during paint application (undesired polymerization) (ACEA, 2014).

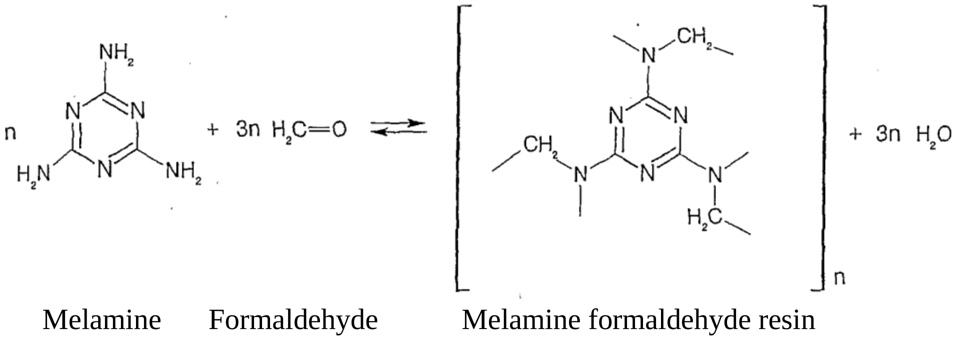

Figure 5. Chemical representation of melamine formaldehyde resin production.

The exact amounts of melamine formaldehyde resin and free formaldehyde in paints is usually not provided by the paint manufacturers if it does not exceed the legal thresholds which oblige them to disclose this information in the Material Safety Datasheets of the paints (Regulation (EC) No 1907/2006). Nevertheless, representative values have been provided by a paint manufacturer in the framework of this study and were collected for the inventory data necessary to carry out the Life Cycle Assessment (see chapter 3). The concentration ranges for the different paints are shown in Table 2.

Table 2. Typical formaldehyde concentrations in vehicle paints.

Paint type	**Melamine resin* in paint wt. %**
Electrocoating	0
Primer surface	0.5 – 7
SB basecoats	0.5 – 10
WB basecoats	0.1 – 9
Clearcoats	10 – 16

* Melamine resins contain between 0.2 and 2.8 % of free formaldehyde. Formaldehyde concentration in paints with melamine resins is generally < 0.3 wt.%

According to this information, formaldehyde is present in automotive coatings as a residue associated with the resin manufacturing process but also as a component bound in melamine polymers.

1.4.2 The formaldehyde emissions

Considering the presence of formaldehyde in vehicle paints and its high volatility, releases of this substance into the atmosphere can be expected. Mainly, emissions of formaldehyde can occur in two different ways:

- Firstly, a small percentage of free formaldehyde present in the paints can be emitted to the atmosphere through the exhaust air coming directly from the paint booths. Based on the concentrations of melamine formaldehyde resins in the different coating steps applied, emissions of formaldehyde can be expected from primer, basecoat and clearcoat spray booths.
- Secondly, during the paint curing process inside the drying ovens at high temperatures the melamine-formaldehyde structure is broken, releasing formaldehyde which will be emitted to the atmosphere if no air emissions abatement equipment is installed or if the

abatement system is not able to completely eliminate the formaldehyde (Salthammer et al., 2010; Salthammer, 2019).

Figure 6 represents this hypothesis:

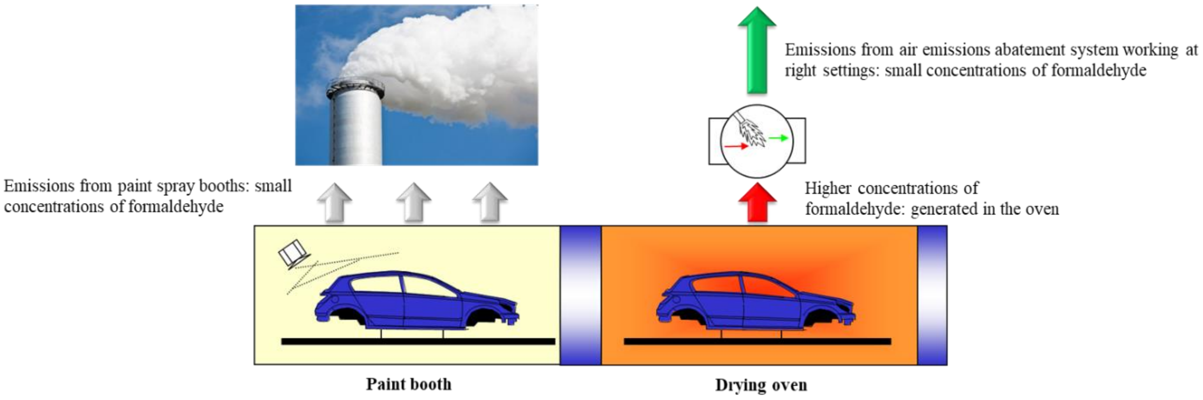

Figure 6. Simple representation of formaldehyde emission sources in paint shop.

Formaldehyde concentrations in the range from 0.2 mg/m^3 to 19 mg/m^3 were observed in internal measurement campaigns conducted in paint shops of different car manufacturers located in Germany (VDA, 2015). However, the emissions of formaldehyde from vehicle paint shops have not been comprehensively studied yet as the absence of publications in this field suggests. The hypothesis represented in Figure 6 was analyzed in-depth in this work and constitutes one of the main objectives and parts of this Ph.D. thesis. This study is developed in chapter 2.

1.4.3 Applicable legislation

The Regulation (EC) No 1272/2008 of the European Parliament and of the Council on “classification, labelling and packaging of substances and mixtures” (so called CLP Regulation) has the main purpose to ensure a high level of protection of human health and the environment by harmonizing the criteria for classification of substances and mixtures, and the rules on labelling and packaging for hazardous substances and mixtures. To reflect the adaptions to technical and scientific progress, this regulation needs to be constantly revised and corrected, thus the classification of chemicals is regularly updated, and new substances can be reclassified as hazardous.

Furthermore, the Directive 2010/75/EU on industrial emissions (so called Industrial Emissions Directive) establishes the rules of integrated pollution prevention and control from industrial activities and is applicable to the industrial processes associated with vehicle painting. This Directive requires the operators to replace, as far as possible, hazardous substances with less harmful substances. In addition, it sets Emission Limit Values (ELV) for carcinogens, mutagens, or substances toxic to reproduction.

In one of the Adaptions to Technical Progress of the CLP Regulation in 2015 (Regulation (EU) No 605/2014; Regulation (EU) No 2015/491), formaldehyde was reclassified to receive the Hazard Statements H350, may cause cancer, and H341, suspected of causing genetic defects. Owing to this higher cancer-causing classification, operators shall replace formaldehyde with less harmful substances and, if the emissions cannot be avoided, compliance with a more stringent ELV of 2 mg/m^3 must be guaranteed. This change forces vehicle manufacturers to evaluate their legal situation and to implement technical and operational countermeasures to reduce or eliminate formaldehyde emissions.

1.4.4 Options for formaldehyde emissions reduction

1.4.4.1 Free formaldehyde from spray booths

For the elimination or reduction of formaldehyde emissions, different alternatives can be taken into account. The first and most sustainable option is the substitution of this substance in the paints and other coating materials. As part of this work, workshops and discussions with paint manufacturers were conducted in order to identify possibilities for the substitution.

Concerning the elimination of the emissions of free formaldehyde from the spray booths, the purification of the paints to reduce the concentration of free formaldehyde is the most suitable countermeasure. Considering that free formaldehyde is present in the paints due to its content of melamine formaldehyde resins, an improvement of the manufacturing processes of the resin to eliminate impurities of formaldehyde is the most preferable option selected by the paint manufacturers. On the other hand, the substitution of the melamine resins in the paint is a much more complex and time-consuming project which implies years of research. This option is currently not possible as indicated by paint manufacturers.

A comparison of the paints´ composition disclosed in the Material Safety Datasheet before and after the reclassification of formaldehyde (Regulation (EU) No 605/2014; Regulation (EU) No 2015/491) demonstrates that the paint manufacturers reduced the amounts of free formaldehyde in their paints due to the reclassification. In Figure 7, an example of the MSDS of a paint before the formaldehyde reclassification (Hazardous Statement: H351) is shown. The MSDS of similar paints analyzed after the reclassification of formaldehyde (Hazardous Statement: H350 and H341) did not show the presence of this substance, demonstrating that the paint manufacturer reduced its concentration below 0.1 % in weight and thus avoiding its disclosure in the MSDS.

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Figure 7. Example of a Material Safety Datasheet from a paint with free formaldehyde in its composition.

1.4.4.2 Formaldehyde released from drying ovens

In order to eliminate or reduce formaldehyde emissions from the drying ovens, two alternative technologies can be considered, which correspond to the abatement technologies commonly installed in the vehicle paint shops across the world for the elimination of VOC emissions. The first option is the installation of a regenerative thermal oxidizer (RTO). The second alternative is the recuperative thermal oxidation. Both types of technology can treat all waste gases from the ovens and are based on the principles of thermal oxidation.

The main component of a thermal oxidizer is a nozzle-stabilized flame maintained by a combination of auxiliary fuel (usually natural gas), waste gas compounds, and supplemental air added when necessary. When the waste gas passes through the flame, it is heated from its inlet temperature (≈100 °C as it leaves the ovens) to its ignition temperature, which depends on the composition of the waste gas. Thus, any organic/air mixture will ignite if its temperature is raised to a sufficiently high level. The mixture continues to react as it flows through the combustion chamber (Sorrels et al., 2017).

Not only the temperature determines the efficiency of the oxidation, but also the time the waste gas takes to pass through the combustion chamber (residence time) plays an important role in the oxidation process. The shorter the residence time, the higher the reactor temperature must be to achieve a certain level of efficiency. For instance, a destruction efficiency of 95 % for toluene can be achieved at 732.8 °C with 0.5 seconds of residence time. If the residence time is increased to one second, the same efficiency could be achieved with a lower temperature of 713.9 °C. To achieve a 99 % destruction efficiency with a residence time of 0.5 seconds, the operating temperature would have to be increased to 744.4 °C. The nominal residence time is defined as the volume of the combustion chamber divided by the volumetric flow rate of the gas. Most commercial units are designed for no more than 1 second of residence time with typical combustion temperatures of 650 °C to 1100 °C. Once the unit is designed and installed, the residence time is not easily changed. Therefore, the temperature is typically the parameter that the operator sets up depending on the composition of the waste gas and the required destruction efficiency (Sorrels et al., 2017).

The use of thermal oxidation for the elimination of VOC emissions leads to environmental cross-media effects (STS BREF, 2020). Apart from the natural gas necessary to operate the equipment, noise and emissions of CO, CO_2 and NOx occur. Figure 8 shows the trend line of CO, total carbon (VOCs) and NOx emitted from a thermal oxidizer in relation to the operating temperature of the combustion chamber. Formaldehyde emissions can be related to the total carbon emissions.

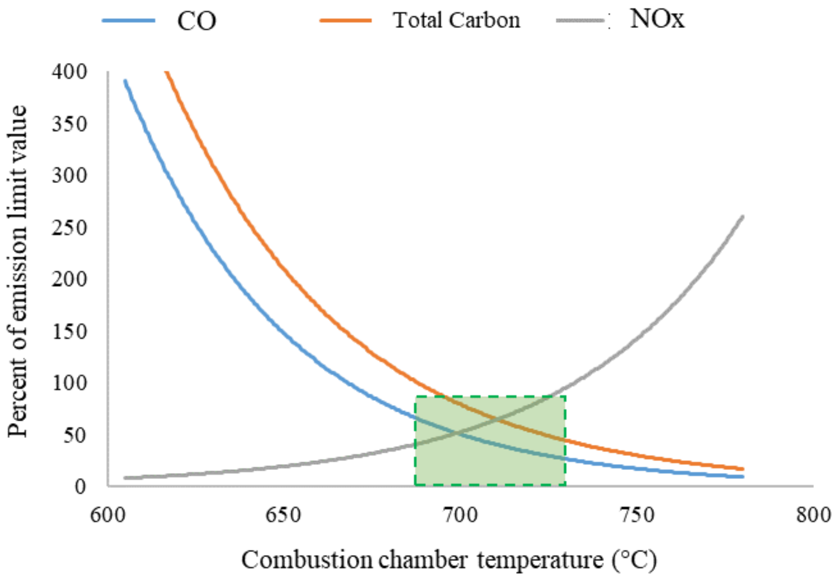

Figure 8. Trend line of CO, total carbon and NOx in relation to the temperature of the combustion chamber inside of a thermal oxidizer. Adapted data from VDI guideline 3455:2013-08. This illustration was elaborated for a simple thermal oxidizer and the temperature values vary for the different technologies described in this work.

While CO follows the same trend as total carbon (VOCs), NOx has an opposite behavior. The higher the temperature of the combustion chamber, the lower the amount of CO and total carbon emitted. On the contrary, the emissions of NOx increase when the temperature raises. The green square in Figure 8 illustrates the temperature range in which the emissions of the three pollutants remain in their lowest values and represents the ideal temperature conditions to achieve a proper VOC destruction with a right balance between ensuring legal compliance and cost efficiency.

1.4.4.2.1 Regenerative Thermal Oxidation

In regenerative thermal oxidation, organic solvents are oxidized at a temperature between 800°C and 850°C (VDI guideline 3455:2013-08). The inlet gas to be treated enters a first hot bed filled with ceramic medium and is preheated to its ignition temperature before entering the combustion chamber. If the desired temperature cannot be achieved, additional auxiliary fuel, i.e. natural gas, is added in the combustion chamber (Sorrels et al., 2017). The first bed is cooled down while the gas is heated. The hot gas reacts in the combustion chamber and continues its course into the second bed, releasing energy and thus heating the ceramic packing of the second bed. The clean gas is then cooled down and released into the atmosphere. The process is carried out alternately so that in the next cycle, the inlet gas is preheated in the second bed and the first bed is where the hot gas is cooled.

Using ceramic materials, the heat is stored and most of the energy produced by combustion is reused in the system itself without the need for additional heat exchangers (VDI guideline 3455:2013-08). This cyclic process achieves very high energy recovery. This reduces the auxiliary fuel requirements and saves operating cost. The destruction efficiency of the regenerative thermal oxidation is 95-99 % (STS BREF, 2020).

Figure 9 shows the main air flows of a simple (2-bed) Regenerative Thermal Oxidizer (RTO).

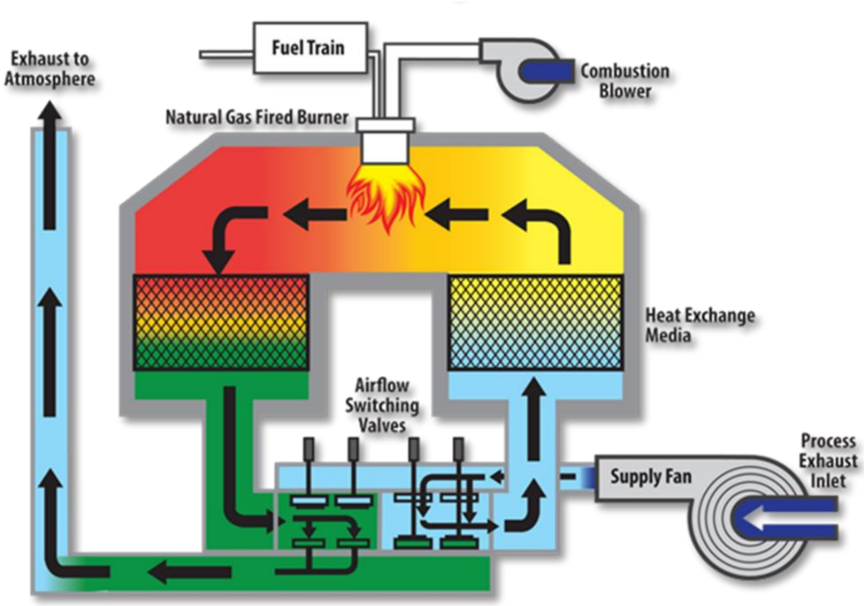

Figure 9. Representation of a simple Regenerative Thermal Oxidizer – Airflow diagram.
(CMM, http://www.thecmmgroup.com).

The typical RTOs use conventional (butterfly or poppet) valves to alternate the airflow direction through the ceramic beds. Since the late 1990s, some RTOs have been designed with rotary valves that reduce the number of moving parts requiring less maintenance (Sorrels et al., 2017).

One problem that arose in RTOs is the release of untreated gas during the switch from one cycle to the next. This has been solved by adding more chambers to the abatement installation, leading to RTOs with three beds, five beds, etc. In these multi-chambered systems, the untreated gas is directed to the idle third chamber and then bled through the combustion chamber instead of going directly to the stack (Sorrels et al., 2017).

Regarding the ceramic packing, several different types of materials are used for RTOs. These include random packing with ceramic saddles, monolithic (honeycomb) structured block and corrugated structure packing. Manufacturers constantly develop new materials and types of ceramic medium to improve their thermal efficiency, pressure drop, corrosion, and plugging or fouling. One important characteristic in new material compositions and shapes is the fact that they can be substituted without modifying the existing unit.

1.4.4.2.2 Recuperative Thermal Oxidation

In recuperative thermal oxidation, the VOCs are oxidized in a simple oxidation chamber by chemical reaction with oxygen present in the exhaust air (STS BREF, 2020). The chamber has an auxiliary burner running on natural gas in which the waste gas is heated up to 700 °C-740 °C, leading to an almost complete oxidation, i.e. a destruction efficiency close to 100 % of the contained organic compounds (VDI guideline 3455:2013-08; STS BREF, 2020).

Recuperative oxidizers have improved their energy efficiency by placing heat exchangers in the hot outlet gas streams. Thus, considerable fuel savings can be obtained by using the heat of the exit gas to preheat the inlet gas, the combustion air, or both via the heat exchangers, which can recover up to 70 % of the energy (enthalpy) in the hot exit gas (Sorrels et al., 2017).

Besides, in vehicle paint shops the energy excess of the clean outlet gas can also be used to heat the drying ovens, which implies an additional benefit of this kind of technology. In these cases, a secondary heat exchanger is necessary.

In Figure 10, the air flows of a common Recuperative Thermal Oxidizer are shown.

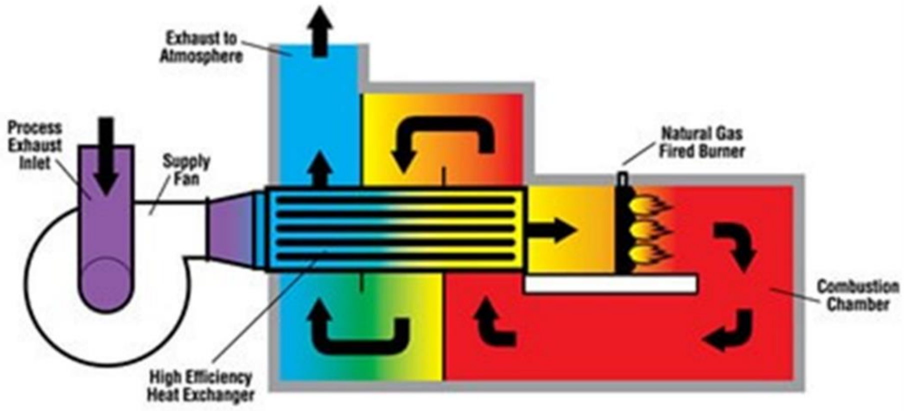

Figure 10. Representation of a common Recuperative Thermal Oxidizer - Airflow diagram. (CMM, http://www.thecmmgroup.com).

1.4.4.2.3 Selection of abatement technology

For the selection of one technology or the other, the advantages and drawbacks of both technologies must be carefully evaluated. Mainly, they can be summarized as follows:

- As far as natural gas consumption is concerned, the installation of recuperative thermal oxidizers is usually considered more convenient since the excess heat can be reused to heat the drying ovens, with the consequent elimination of existing burners and the concomitant savings of natural gas.
- The installation cost of an RTO is typically higher than that of a recuperative oxidizer. However, the treatment of high waste gas volumes might need the installation of several recuperative thermal oxidizers and their associated heat exchangers, while the same amount of waste gas can be treated by only one RTO, just by increasing the number of ceramic beds. This usually leads to higher initial investment costs for the recuperative thermal oxidizers. Maintenance costs are higher for the RTO, mainly due to the regular exchange of the ceramic packing. Generally, the installation of the RTO is more advantageous from an economic point of view.
- For the installation of recuperative oxidizers, longer production shutdown periods are required due to the need to install and connect heat exchangers to recover the excess heat from the abatement systems and use it to operate the drying ovens. On the contrary, an RTO can be built independently and without disturbing the production process and only a few weeks of production shutdown are needed to finally connect the abatement system to the process.
- The RTO is independent to the painting lines and ovens, so that in the event of breakdowns, production can continue without vehicle losses and production delays. Since the excess heat from the recuperative thermal oxidizers would be used to heat the

drying ovens, drying and painting shall be stopped in case of malfunctions and necessary repairs.

A simplified representation of the main differences, advantages and drawbacks of the two alternative systems is shown in table 3.

Table 3. Comparison of the main characteristics of the two alternative abatement systems*.

Main Characteristics	RTO	Recuperative Thermal Oxidizers
Abatement efficiency	95-99 %	≈ 100%
Initial investment costs	Lower	Higher
Maintenance costs	Higher	Lower
Overall natural gas consumption of the paint shop	Higher	Lower due to excess heat recovery to run the ovens
Energy recovery	Internal due to ceramic packing. Often not technically possible to recover excess heat to other paint shop processes	Excess heat recovered to run the ovens
Ability to Run Oven Without Abatement System	Yes	No
Space Utilization	Lower	Higher if several devices are necessary for a given volume flow
Accessibility for Repair or Parts Replacement	Easier	More difficult
Time to install	During production	Not possible during production
Lifespan	Long Life Equipment	It will have to be replaced during life of oven

* This table shows the results of a technical and cost evaluation of the two abatement technologies for the paint shops within the scope of this work and might differ for a paint shop with a different set-up.

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2 INVENTORY OF FORMALDEHYDE EMISSIONS

In chapter 1, the presence of formaldehyde in vehicle paints was explained. In addition, the areas and sub-processes of the paint shop from which emissions of formaldehyde can be expected were briefly described. They can be summarized as follows:

- Small amounts of formaldehyde from waste gas coming from the paint booths of the primer, basecoat and clearcoat processes.
- Higher amounts of formaldehyde in the waste gas coming from the drying ovens.
- Small amounts below applicable legal emission limits after abatement systems installed at the drying ovens.
- Higher emissions of formaldehyde if no abatement equipment is installed or if the abatement system is not able to reduce or eliminate the formaldehyde.

In this chapter, the investigation carried out in this Ph.D. thesis in order to clarify and confirm this hypothesis is described and a proposal for corrective actions to be taken by the company to reduce formaldehyde emissions is given.

2.1 OBJECTIVES

The main objectives of this chapter are:

- Describe the elaboration of the measurement programs for the six paint shops studied.
- Introduce the methodologies applied to carry out the measurements.
- Confirm the hypothesis made in chapter 1 regarding the areas and sub-processes in the paint shop where formaldehyde emissions occur.
- Identify the areas and plants that need corrective action to ensure legal compliance with emission limit values.
- Identify possible corrective actions and propose actions for implementation to the company.

- Collect the inventory data regarding formaldehyde emission values for the LCA developed in chapter 3.
- Provide input for the decision-making process carried out by the company considering the environmental sustainability perspective.

2.2 SCOPE

Measurements of formaldehyde at the relevant chimneys of the company´s six paint shops described in chapter 1 were carried out. The list of paint shops studied is as follows:

Section affected by copyright protection.

The entire painting process and the different sub-processes were described in chapter 1. Based on the information provided by paint manufacturers in relation to the formaldehyde contents of the various painting materials, as explained in chapter 1, the scope of the measurements could be narrowed down to the relevant processes for which formaldehyde emissions can be expected. Therefore, the scope of the measurement programs in these six paint shops can be simplified to the following sub-processes and areas of the paint shop.

- Primer booth emissions
- Primer flash off zone
- Primer ovens
- Basecoat spray booth emissions
- Basecoat intermediate flash off zone
- Clearcoat spray booth emissions
- Topcoat ovens

Additionally, the emissions from the electrocoating bath and electrocoating ovens were also included in the measurement programs to identify whether formaldehyde is also present in this sub-process.

In most cases, additional sub-processes such as sealing or wax application were left out of the measurement program. They were considered as not relevant with regard to *the formaldehyde emissions problem*. Only in some specific cases the emissions of these additional sub-processes were included in the measurements to obtain a confirmation that formaldehyde is not emitted from such processes and that they can be neglected.

2.3 METHODOLOGY

In this section, the elaboration of the measurement program for each of the six plants is explained as well as the methods applied to carry out the measurements. The emission sources were selected individually for each plant at which the measurements were carried out. The selection was based on a thorough analysis of all emission sources of the plants and considering the potential formaldehyde emissions expected, in collaboration with paint shop and environmental engineers of the company´s central offices and the plant. The measurements were conducted by local measuring institutes available in the region where the plants are located. Contracts with the six measuring companies were made and they included the emission sources and the measuring conditions in the scope of work. At the time the measurements were being carried out, several parameters were collected to ensure that all relevant information necessary to evaluate the results was available. The main parameters are:

- Temperature of the abatement systems.
- Temperature of the drying ovens.
- Paints, solvents and other materials applied during the measurements. This includes the Safety Data Sheets of the materials.
- Utilized capacity, i.e., the number of vehicles that are being painted and dried per hour during the measurements.

In the following sections, the measurement programs of the six paint shops are shown.

2.3.1 Measurement programs

2.3.1.1 Paint shop 1

Section affected by copyright protection. The first measurement program elaborated was for paint shop 1. In this plant, only the emission sources to the atmosphere (chimneys) were considered and no intermediate measurement point was selected, e.g., before treatment in abatement installation. This was decided since the first objective was to determine whether formaldehyde is emitted to the atmosphere and which emission values are observed. The sub-processes selected for the measurement program are electrocoating, primer and topcoat. In Table 4 a summary of the selected emission points is shown, including the description of the process related to the emission point, the abatement equipment temperature and the utilized capacity of the paint shop at the time of the measurements.

Table 4. Measurement program for paint shop 1.

Measurement point designation	Process related	Abatement Temperature °C	Operating conditions (utilized capacity %)
	Electrocoating abatement treated waste gas	720	94
	Electrocoating abatement treated waste gas	710	85
	Primer and Topcoat Paint booths	-	84
	Topcoat line 2 abatement treated waste gas	695	73
	Topcoat line 2 abatement treated waste gas	695	79
	Topcoat line 3 abatement treated waste gas	695	52
	Topcoat line 3 abatement cleaned gas	695	58
	Primer line 1 abatement treated waste gas	720	73
	Primer line 2 abatement treated waste gas	720	73
	Primer line 3 abatement treated waste gas	720	73

2.3.1.2 Paint shop 2

Section affected by copyright protection. In the next paint shop, the decision was made to include the exit points from the ovens before they enter the abatement systems. With this approach, the release of formaldehyde in the ovens can be evaluated and confirmed. This strategy was also followed in the next paint shops. Table 5 shows the measurement program for this paint shop.

Table 5. Measurement program for paint shop 2.

Measurement point designation	Process related	Abatement Temperature °C	Operating conditions (utilized capacity %)
	Electrocoating oven exit before abatement	702	84
	Electrocoating abatement treated waste gas	702	84
	Primer oven 1 exit before abatement	712	84
	Primer oven 1 abatement treated waste gas	712	84
	Primer oven 2 exit before abatement	712	84
	Primer oven 2 abatement treated waste gas	712	84
	Primer cooling zone	N/A	84
	Topcoat oven 1 exit before abatement	706	78
	Topcoat oven 1 abatement treated waste gas	706	78
	Topcoat oven 2 exit before abatement	706	80
	Topcoat oven 2 abatement treated waste gas	706	80
	Topcoat oven 3 exit before abatement	706	-
	Topcoat oven 3 abatement treated waste gas	706	-
	Topcoat cooling zone	N/A	91
	Spray booths	N/A	80

2.3.1.3 Paint shop 3

Section affected by copyright protection. As can be seen in the description of the paint shop conditions in chapter 1, this paint shop has a high number of chimneys and measuring points, each of them dedicated to small areas or zones of the paint shop processes. For this reason, a selection had to be made to carry out the measurements in the most representative emission points of the different sub-processes and thus reducing the measurements time and costs. In cases where several abatement installations were installed for the same oven, only the emissions from one installation were considered. In cases where several chimneys discharge the emissions from the same sub-process, only a reduced number of chimneys was selected and were considered as representative of the system. In Table 6 the emission points selected for the measurements in this paint shop are shown.

Table 6. Measurement program for paint shop 3.

Measurement point designation	Process related	Abatement Temperature °C	Operating conditions (utilized capacity %)
	Electrocoating oven exit before abatement	675	87
	Electrocoating abatement treated waste gas	675	87
	Electrocoating abatement treated waste gas	675	87
	Primer Flash off	N/A	76
	Primer line 2 cooling zone	N/A	93
	Primer line 1 oven exit before abatement	540	83
	Primer line 1 abatement treated waste gas	540	85
	Primer line 1 oven exit before abatement	540	83
	Primer line 1 abatement treated waste gas	540	85
	Primer line 1 oven exit before abatement	540	83
	Primer line 1 abatement treated waste gas	540	85
	Topcoat line 2 flash off	N/A	100
	Topcoat 1 oven hold zone (no abatement)	N/A	91
	Topcoat 2 oven heat up zone (no abatement)	N/A	98
	Topcoat 2 oven hold zone (no abatement)	N/A	98
	Topcoat 2 cooling zone 1 (no abatement)	N/A	98
	Topcoat 2 cooling zone 2 (no abatement)	N/A	98
	Topcoat 3 oven hold zone (no abatement)	N/A	80
	Basecoat paint booth	N/A	85
	Basecoat paint booth	N/A	85
	Basecoat paint booth	N/A	85
	Basecoat paint booth abatement treated waste gas	-	93
	Basecoat paint booth abatement treated waste gas	-	93
	Basecoat paint booth abatement treated waste gas	-	93
	Basecoat clean air after Zeolite adsorption	N/A	84
	Basecoat spray booth VOC concentrated before abatement	-	60
	Basecoat spray booth abatement treated waste gas	-	89

2.3.1.4 Paint shop 4

Section affected by copyright protection. The measurement program for this paint shop is similar to the program developed for the paint shop 1 since the type of paint shop and chimney profile is similar. As can be seen in Table 7, the concentrations of formaldehyde were also measured before and after the abatement systems in order to confirm the formaldehyde release in the ovens and the elimination or reduction in the abatement installation.

Table 7. Measurement program for paint shop 4.

Measurement point designation	Process related	Abatement Temperature °C	Operating conditions (utilized capacity %)
	Cab painting - base coat painting, Cathodic immersion process Electrocoating, Paint mix, Evaporation between operations, Working platforms, Coagulation area.	N/A	82
	Cab chassis protection, Cab paint primer (Primer), Cab painting - Clear coat, local repair, tilting, removal of Electrocoating	N/A	82
	Electrocoating oven exit before abatement	710	82
	Electrocoating abatement treated waste gas	710	82
	Primer oven exit before abatement	710	82
	Primer abatement treated waste gas	710	82
	Primer oven exit before abatement	710	82
	Primer abatement treated waste gas	710	82
	Topcoat oven exit before abatement	710	82
	Topcoat abatement treated waste gas	710	82
	Topcoat oven exit before abatement	710	82
	Topcoat abatement treated waste gas	710	82

2.3.1.5 Paint shop 5

Section affected by copyright protection. The measurement program for this paint shop has a difference in comparison to the previous paint shops. Even though formaldehyde is not present in sealing and waxing materials, the chimneys from the sub-processes for the sealing and wax applications were also included in the measurement program to confirm the absence of formaldehyde in the waste gas. Although formaldehyde is not expected from those processes, it was known by the paint shop operators that the ducts and exhaust systems might be interconnected, and leaks of formaldehyde or other VOCs cannot be excluded. In Table 8 the measurement program for this paint shop is shown.

Table 8. Measurement program for paint shop 5.

Measurement point designation	Process related	Abatement Temperature °C	Operating conditions (utilized capacity %)
	PVC application 1	N/A	70
	PVC application 2	N/A	70
	Cavity wax application 1	N/A	70
	Cavity wax application 2	N/A	70
	Cavity wax application 3	N/A	70
	Final Wax application 1	N/A	70
	Final Wax application 2	N/A	70
	Primer and Topcoat spray booth waste gas	N/A	70
	Electrocoating oven 1 exit before abatement	712	70
	Electrocoating oven 2 exit before abatement	712	70
	Electrocoating abatement 1 treated waste gas	712	70
	Electrocoating abatement 2 treated waste gas	712	70
	Primer oven exit before abatement 1	702	70
	Primer abatement 1 treated waste gas	702	70
	Primer oven exit before abatement 2	695	70
	Primer abatement 2 treated waste gas	695	70
	Topcoat oven exit before abatement	840	70
	Topcoat abatement treated waste gas	840	70

2.3.1.6 Paint shop 6

Section affected by copyright protection. The measurement program for this paint shop was developed following the strategy of paint shop 1. For simplicity, only the direct emission points into the atmosphere were considered for the measurement program and any additional measurement before the abatement systems was excluded. This has been extensively analyzed for paint shops 2 to 5 and therefore it was not necessary to include such measurement in paint shop 6. The measurement points selected for paint shop 6 are shown in the Table 9.

Table 9. Measurement program for paint shop 6.

Measurement point designation	Process related	Abatement Temperature °C	Operating conditions (utilized capacity %)
	Electrocoating abatement treated waste gas	810-815	95
	Primer spray booth	N/A	95
	Primer abatement treated waste gas	815	95
	Topcoat spray booth	N/A	95
	Topcoat flash off	N/A	95
	Topcoat abatement treated waste gas	720	95
	Spray booth special vehicles painting	N/A	95
	Oven special vehicles painting exit after abatement	760	95

2.3.2 Methodology for formaldehyde measurements

The measuring companies selected to perform the measurements must have the necessary accreditation to conduct the sampling and analysis for emissions measurements of formaldehyde. They must also have experience with the sampling since this is a complex procedure which, if not done correctly, can influence the results. For this reason, the selection of the measuring company was made under a thorough evaluation, and in some cases, companies were excluded from the selection as they did not comply with the established quality requirements. In specific cases, a subcontractor was engaged by the measuring company for the analysis of the samples in the laboratory. In this case, this company must also have the corresponding accreditation for the formaldehyde analysis.

For the sampling of the waste gases, a difference between legal measurements and internal measurements must be made. Depending on the country legal requirements, the sampling might differ with regard to the sampling time. In general, taking three samples of 1 hour is the common procedure applied in legally required measurements. Since the formaldehyde measurements carried out in this work were internal measurements, a simplification of this procedure was applied in some of the paint shops in order to reduce the measurements time and the costs. In those cases, either the sampling time of the three samples was reduced to 30 minutes or only two samples of 1 hour were taken.

The concentration of formaldehyde in the waste gas of the chimneys (emissions measurements) can be determined by different methodologies. The results obtained by the different methodologies are equivalent, being the main difference the sensitivity of the method. While one method is more suitable for measurements in ambient air, another method is more accurate when applied in waste gas from a chimney. The different measuring institutes applied the methodology they were accredited for. Nevertheless, the results were considered comparable regardless of the method by the paint shop and environmental engineers of the company as well as by the measuring company technicians. In specific cases, to validate the results, the first results obtained by applying one method were confirmed by applying a second method in the same paint shop under similar operating conditions.

The different methods applied for the determination of the formaldehyde concentrations are described in the following sections.

2.3.2.1 DNPH Method – Impinger Method

The most common method for the determination of formaldehyde in waste gases applied by measuring companies in industrial processes is the DNPH method – Impinger method (VDI 3862 Part 2:2000-12). This method is typically used for the measurements of aliphatic and aromatic aldehydes and ketones in gas and wood firing installations, gas turbines, internal combustion engines and smoking facilities.

In this method, the gaseous emissions are drawn into an impinger that contains an aqueous solution of 2,4-dinitrophenyl-hydrazine (DNPH). The samples taken on the field are subsequently brought to the laboratory for further analysis. Formaldehyde reacts with DNPH to form 2,4-dinitrophenylhydrazone. After extraction with an organic solvent, the samples are analyzed using HPLC to quantify the formaldehyde concentrations by analyzing the retention times and area counts of sample extracts with those of standard solutions.

2.3.2.2 XAD-2 Collection Tubes Method

This methodology is equivalent to the DNPH method, but with the difference that instead of DNPH, formaldehyde reacts with 2-(hydroxymethyl) piperidine on a XAD-2 sorbent bed installed in sample collection tubes (EkoNorm communication, 2015). Regarding determination of formaldehyde in the samples, this method uses HPLC as in the DNPH method.

2.3.2.3 Multicomponent FTIR Gas Analyzer

This method is typically used for continuous monitoring of formaldehyde, CO, NO, and NO_2 in which the stationary equipment necessary for the measurements is permanently installed. In certain circumstances, this equipment can be installed only during the measurements campaign. This method is commonly used by manufacturers of paint shop equipment in order to analyze the efficiency of their installations, e.g., abatement systems. This method is not commonly used by measuring companies (ECA communication, 2015).

In this method, when infrared radiation passes through a measuring cell containing an infrared active gas, the energy attenuates to a greater or lesser extent at certain wavelengths as the infrared radiation is absorbed by the molecules. Considering the strength of the absorption as well as the wavelength range in which absorption takes place, a large number of organic and inorganic gases and their concentration in the gas mixture can be determined. With the aid of an interferometer, the contribution of the individual wavelengths of the broadband infrared radiation can be measured. The calculation of the spectra from the interferometer data takes place by the fast Fourier transformation. When analyzing the measurement spectrum, the spectra of the individual gases are analyzed, and the concentrations of the different gases present in the sample can be calculated (Dürr report, 2016).

2.4 RESULTS AND DISCUSSION

Section affected by copyright protection.

Once all measurement programs were defined and the contracts with the measuring companies were established, the formaldehyde measurements were performed in each individual paint shop. The results obtained for each plant as well as their interpretation and discussion are given in this section.

Based on the results, the emissions of formaldehyde from the painting process can be understood and the hypothesis stated in chapter 1 related to the sources for formaldehyde emissions into the atmosphere can be validated and confirmed. In specific cases, measurements were repeated under different operating conditions in order to evaluate the formaldehyde emissions in more detail or achieve a more in-depth knowledge on how the emissions vary depending on the settings of the paint shop processes.

2.4.1 Paint shop 1

Table 10 shows the results obtained for the paint shop 1. The measurements in this paint shop only include the direct emissions from chimneys into the atmosphere.

Table 10. Measurement results for paint shop 1.

Process related	Abatement Temperature °C	Average Formaldehyde concentration mg/m^3	Measurement uncertainty (95%) mg/m^3
Electrocoating abatement treated waste gas	720	0.8	0.2
Electrocoating abatement treated waste gas	710	<0.1	0.2
Primer and Topcoat Paint booths	-	0.2	0.2
Top coat line 2 abatement treated waste gas	695	0.1	0.2
Top coat line 2 abatement treated waste gas	695	0.1	0.2
Top coat line 3 abatement treated waste gas	695	0.3	0.2
Top coat line 3 abatement cleaned gas	695	<0.1	0.2
Primer line 1 abatement treated waste gas	720	0.5	0.2
Primer line 2 abatement treated waste gas	720	1.0	0.2
Primer line 3 abatement treated waste gas	720	0.7	0.2

Evaluating these results, two important aspects can be seen. Firstly, the formaldehyde concentration observed in the emissions from the primer and topcoat paint booths is 0.2 mg/m^3. This value is far below the European applicable emission limit value of 2 mg/m^3 (Directive 2010/75/EU), confirming that the emissions of free formaldehyde from the usage of paints in the spray booths are low. The second observation is the fact that the emissions from the treated waste gas of the ovens after the abatement equipment are higher than those from the paint booths. For instance, in the primer lines, the concentration values are in the range of 0.5-1.0 mg/m^3. This result suggests that inside the ovens the concentration of formaldehyde increases to a certain extent, providing a first evidence that formaldehyde is released in the ovens due to the presence of melamine resins in the paints. However, as a consequence of the oxidation in the abatement system, the amount of formaldehyde is reduced to values which are still below the applicable emission limit. Furthermore, considering that the abatement technology applied in this paint shop is recuperative thermal oxidation, it can also be concluded that the operation of this technology with temperatures close to 700 ºC and higher is sufficient to achieve a formaldehyde reduction below the legal emission limits.

2.4.2 Paint shop 2

The results obtained for paint shop 2 can be seen in Table 11. In this paint shop, additional intermediate points were selected for the measurements even if they are not direct discharges into the atmosphere. Specifically, samples of the waste gas from the ovens before it enters the abatement system for treatment were taken and the formaldehyde concentrations were determined.

Table 11. Measurement results for paint shop 2.

Process related	Abatement Temperature °C	Average Formaldehyde concentration mg/m^3	Measurement uncertainty (95%) mg/m^3
Electrocoating oven exit before abatement	702	10.4	0.4
Electrocoating abatement treated waste gas	702	0.6	0.1
Primer oven 1 exit before abatement	712	9.4	0.4
Primer oven 1 abatement treated waste gas	712	0.2	0.01
Primer oven 2 exit before abatement	712	11.7	0.5
Primer oven 2 abatement treated waste gas	712	< 0.1	< 0.1
Primer cooling zone	N/A	< 0.1	< 0.1
Topcoat oven 1 exit before abatement	706	62.7	0.3
Topcoat oven 1 abatement treated waste gas	706	0.5	0.1
Topcoat oven 2 exit before abatement	706	88.3	3.6
Topcoat oven 2 abatement treated waste gas	706	0.2	0.01
Topcoat oven 3 exit before abatement	706	11.9	0.5
Topcoat oven 3 abatement treated waste gas	706	< 0.1	< 0.1
Topcoat cooling zone	N/A	0.5	0.02
Spray booths	N/A	0.1	0.01

The results obtained in this paint shop confirm what was observed in paint shop 1 regarding the emissions of free formaldehyde from the spray booths. In this case, a formaldehyde concentration of 0.1 mg/m^3 can be seen for the spray booths, which is comparable to that of paint shop 1 (0.2 mg/m^3) and significantly below the applicable emission limit. On the other hand, high concentrations can be seen at the exit of the ovens prior to the treatment in the abatement system. This behavior is observed in all sub-processes. As an example, the results of the primer ovens are 9.4 mg/m^3 and 11.7 mg/m^3, respectively, before the abatement system and 0.2 mg/m^3 and <0.1 mg/m^3 after the treatment. An even more significant difference can be identified at the topcoat ovens, with concentration values before the abatement systems of 62.7 mg/m^3, 88.3 mg/m^3 and 11.9 mg/m^3, respectively, and lower than 1 mg/m^3 after the abatement system. These results confirm the release of formaldehyde in the drying ovens due to the use of melamine resins and the destruction of this substance in the abatement system working at temperatures greater than 700 ºC. In this case, similar to paint shop 1, recuperative thermal oxidizers are installed for the reduction of VOCs.

An unexpected result was obtained for the electrocoating process. According to paint manufacturers, the materials used in this process do not contain melamine resins. Despite of that the concentrations of formaldehyde observed after the oven and before the abatement system are surprisingly high (10.4 mg/m^3). This result led to an additional investigation of the electrocoating process and discussions with paint shop engineers. Even though the resins used in the electrocoating process are not melamine resins, it is suspected that formaldehyde residues might be present in the materials used in the electrocoating baths and can be released during the curing process, causing the high formaldehyde concentrations after the oven. In any case, the abatement system connected to the electrocoating ovens is able to reduce the formaldehyde emission below the legal emission limits.

Additionally, a formaldehyde concentration of 0.5 mg/m^3 was observed for the topcoat cooling zone. The cooling zone is the area in which the painted bodies are cooled down after the oven. The exhaust air from this area might be treated in the abatement system of the oven or directly discharged into the atmosphere, depending on the configuration of the paint shop. The concentration value obtained from the cooling zone confirms that this substance is released at temperatures greater than the ambient temperature and therefore the values are higher than those from the spray booths. Nevertheless, the emissions of formaldehyde from this area are below the legal emission limit even if this waste gas is directly discharged into the atmosphere.

2.4.3 Paint shop 3

The results of the measurements conducted in paint shop 3 are shown in Table 12. Like paint shop 2, several points before treatment in an abatement system were selected to confirm the release of formaldehyde in the drying ovens. As shown in chapter 1, the main difference of this paint shop compared to the others is the presence of abatement equipment for the waste gas of the basecoat spray booths and the fact that the topcoat ovens do not have an abatement system installed. Thus, if formaldehyde is released in the ovens, high concentrations of formaldehyde are expected in the oven waste gas.

Table 12. Measurement results for paint shop 3.

Process related	Abatement Temperature °C	Average Formaldehyde concentration * mg/m^3
Electrocoating oven exit before abatement	675	0.031
Electrocoating abatement treated waste gas	675	0.71
Electrocoating abatement treated waste gas	675	0.22
Primer Flash off	N/A	3.4
Primer line 2 cooling zone	N/A	1.16
Primer line 1 oven exit before abatement	540	12.26
Primer line 1 abatement treated waste gas	540	9.71
Primer line 1 oven exit before abatement	540	10.74
Primer line 1 abatement treated waste gas	540	10.01
Primer line 1 oven exit before abatement	540	4.37
Primer line 1 abatement treated waste gas	540	9.04
Topcoat line 2 flash off	N/A	1.84
Topcoat 1 oven hold zone (no abatement)	N/A	12.34
Topcoat 2 oven heat up zone (no abatement)	N/A	13.95
Topcoat 2 oven hold zone (no abatement)	N/A	10.11
Topcoat 2 cooling zone 1 (no abatement)	N/A	0.08
Topcoat 2 cooling zone 2 (no abatement)	N/A	0.09
Topcoat 3 oven hold zone (no abatement)	N/A	14.23
Basecoat paint booth	N/A	0.42
Basecoat paint booth	N/A	0.04
Basecoat paint booth	N/A	0.26
Basecoat paint booth abatement treated waste gas	Not known	0.45
Basecoat paint booth abatement treated waste gas	Not known	0.08
Basecoat paint booth abatement treated waste gas	Not known	0.05
Basecoat clean air after Zeolite adsorption	N/A	0.27
Basecoat spray booth VOC concentrated before abatement	Not known	1.71
Basecoat spray booth abatement treated waste gas	Not known	0.16

* 15 % Measurement Uncertainty

The observations made for paint shops 1 and 2 can also be confirmed for paint shop 3. Besides, additional information was obtained from the measurement results of this paint shop.

Firstly, the emissions from the spray booths are low, with concentration values below 0.5 mg/m^3. This can be seen, for instance, in the basecoat spray booth measurement results (0.42, 0.04 and 0.26 mg/m^3, respectively). In addition, the value observed in the exhaust air of the VOC concentration system (1.71 mg/m^3) before the recuperative thermal oxidizer installed for the basecoat spray booth is higher than those from the basecoat spray booth. This behavior is plausible since the VOCs, including formaldehyde, are concentrated prior to their treatment in the abatement system. However, the emission values to the atmosphere after the treatment are low (0.45, 0.08 and 0.05 mg/m^3, respectively), confirming that the abatement installation is reducing formaldehyde to levels below the applicable emission limit value.

The flash off zones are intermediate tunnels where the solvents start to evaporate before the vehicle body enters the oven. They operate at temperatures in the range of 50ºC to 70ºC. The concentration results obtained in the waste gas from these areas, i.e., primer flash off (3.4 mg/m^3) and topcoat line 2 flash off (1.84 mg/m^3), suggest that at these temperatures, significant amounts of formaldehyde are already released.

With regard to the ovens, the results confirm the observations previously made in paint shops 1 and 2. The emissions observed for the electrocoating oven are reasonable. Due to the use of recuperative thermal oxidizers with an operating temperature of 675 ºC to treat the waste gas from the oven, the concentrations of formaldehyde can be reduced to values lower than the applicable emission limit (0.71 and 0.22 mg/m^3, respectively). However, when it comes to the primer and topcoat ovens, the results indicate that, when the operating temperature of the abatement systems is low or no abatement equipment is installed, the emissions of formaldehyde cannot be reduced, and the applicable emission limit value cannot be met. This behavior is confirmed by the results obtained for the primer oven. The recuperative thermal oxidizers connected to this oven operate at 540 ºC. The formaldehyde concentrations obtained for the exhaust gas after the treatment are in the range from 4.37 to 12.26 mg/m^3, and thus higher than the applicable emission limit value. These results demonstrate that this temperature is not sufficient to reduce the formaldehyde concentration adequately. A more critical situation can be seen for the topcoat ovens, which do not have an installed abatement equipment. The formaldehyde concentrations are between 10.11 mg/m^3 and 14.23 mg/m^3. These values confirm again that formaldehyde is released in the drying ovens and without an abatement system, the emissions are higher than the applicable emission limit value.

The results observed for the emissions after the abatement systems of the primer ovens led to an additional investigation. The operating temperature of 540 ºC is not sufficient to reduce formaldehyde to low values. Therefore, the temperature of these abatement installations was modified during normal production conditions and measurements at different temperatures were carried out. This investigation allows to obtain the correct temperature at which the formaldehyde concentrations are below the applicable emission limit value. Table 13 shows the measurements results for the exhaust gas of three primer oven abatement installations operating at different temperatures.

Table 13. Measurement results of primer oven abatement systems at different temperatures.

Abatement Temperature ºC	**Abatement system 1 - Line 1** Average Formaldehyde concentration * mg/m^3	**Abatement system 2 - Line 1** Average Formaldehyde concentration * mg/m^3	**Abatement system 3 - Line 1** Average Formaldehyde concentration * mg/m^3
360			10.6
500	3.3	7.7	9.0
550			11.7
600	0.31	0.47	10.4
650	1.8	0.05	6.4
700	1.7	1.7	2.9
730	0.13	0.40	0.14

* 15 % Measurement Uncertainty

These results present some inconsistencies, specifically for the abatement system 1 and 2. As an example, the emissions at 600 ºC are lower than the values observed at 700 ºC (0.31 and 0.47 mg/m^3 against 1.7 and 1.7 mg/m^3, respectively). It is important to bear in mind that the measurements were conducted at real production conditions. This implies significant fluctuations in the number vehicle bodies being painted and the type of paints and colors being applied. Therefore, it might be reasonable that the inconsistencies in these results are due to the fluctuations in the operational conditions. Nevertheless, some conclusions can be drawn from the results. It is obvious that only at temperatures above 700 ºC the emissions of formaldehyde can be reduced to values below the applicable emission limit value. Since the measurements in the abatement system 3 were conducted at seven different temperatures, a representation of these results can better illustrate the decrease of the formaldehyde emissions with the variation of the temperature. Figure 11 shows this representation.

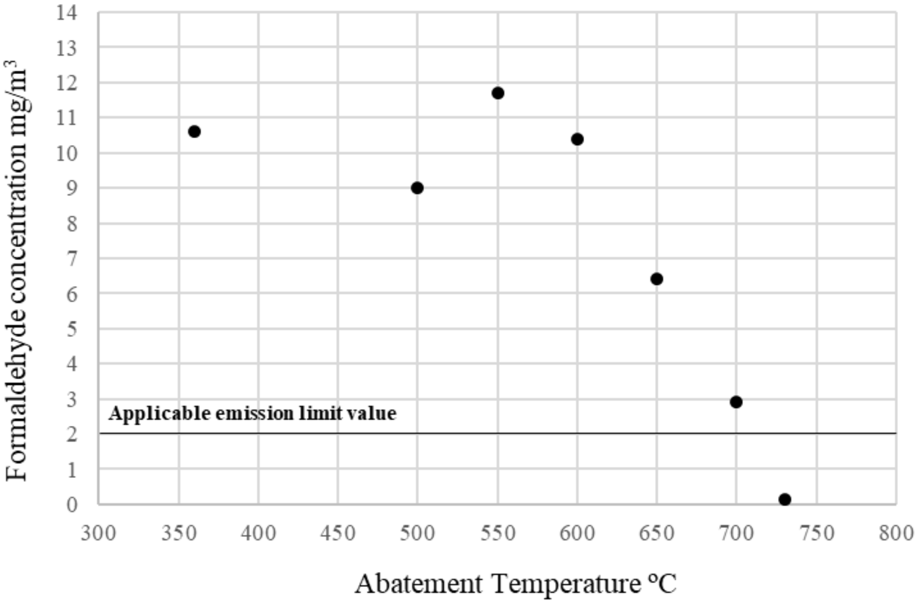

Figure 11. Reduction of formaldehyde emissions with the variation of the operating temperature of the primer oven Abatement system 3 - Line 1.

As can be seen, the reduction of formaldehyde begins at a temperature of 650 ºC, achieving values below the applicable emission limit at temperatures higher than 700 ºC. These results unequivocally demonstrate that only when abatement equipment is installed for the treatment of the oven´s waste gas and this equipment is working at the right temperature, compliance with the emission limit values for formaldehyde can be ensured.

2.4.4 Paint shop 4

Table 14 contains the results obtained for paint shop 4. This paint shop is similar to paint shop 2 regarding its processes and distribution of emission sources.

Table 14. Measurement results for paint shop 4.

Process related	Abatement Temperature °C	Average Formaldehyde concentration mg/m^3	Measurement uncertainty mg/m^3
Cab painting - base coat painting, Cathodic immersion process Electrocoating, Paint mix, Evaporation between operations, Working platforms, Coagulation area.	N/A	0.159	0.019
Cab chassis protection, Cab paint primer (Primer), Cab painting - Clear coat, local repair, tilting, removal of Electrocoating	N/A	0.078	0.009
Electrocoating oven exit before abatement	710	2.182	0.262
Electrocoating abatement treated waste gas	710	-	-
Primer oven exit before abatement	710	3.168	0.38
Primer abatement treated waste gas	710	0.018	0.002
Primer oven exit before abatement	710	2.13	0.26
Primer abatement treated waste gas	710	0.007	0.001
Topcoat oven exit before abatement	710	17.54	2.105
Topcoat abatement treated waste gas	710	0.254	0.03
Topcoat oven exit before abatement	710	4.124	0.495
Topcoat abatement treated waste gas	710	0.066	0.008

The concentration values obtained in this paint shop are like those observed in paint shop 2. The emissions from the spray booths are very low (0.159 and 0.078 mg/m^3, respectively). On the other hand, the concentrations at the exit of the ovens are high with values from 2.13 mg/m^3 (primer) to 17.54 mg/m^3 (topcoat). These emissions are reduced to values below 0.3 mg/m^3 in the respective recuperative thermal oxidizers operating at 710 ºC.

2.4.5 Paint shop 5

In Table 15, the results of paint shop 5 are shown.

Table 15. Measurement results for paint shop 5.

Process related	Abatement Temperature °C	Average Formaldehyde concentration * mg/m^3
PVC application 1	N/A	0.70
PVC application 2	N/A	0.53
Cavity wax application 1	N/A	2.15
Cavity wax application 2	N/A	2.66
Cavity wax application 3	N/A	0.54
Final Wax application 1	N/A	0.53
Final Wax application 2	N/A	0.57
Primer and Topcoat spray booth waste gas	N/A	0.47
Electrocoating oven 1 exit before abatement	712	4.51
Electrocoating oven 2 exit before abatement	712	3.41
Electrocoating abatement 1 treated waste gas	712	4.27
Electrocoating abatement 2 treated waste gas	712	1.19
Primer oven exit before abatement 1	702	7.69
Primer abatement 1 treated waste gas	702	0.31
Primer oven exit before abatement 2	695	5.09
Primer abatement 2 treated waste gas	695	0.99
Topcoat oven exit before abatement	840	4.0
Topcoat abatement treated waste gas	840	2.75

* 12 % Measurement Uncertainty

In this paint shop, PVC and waxing applications were included in the measurement program. The concentrations observed for these areas and particularly for the cavity wax application are unexpectedly high (2.15, 2.66 and 0.54 mg/m^3, respectively). The results were discussed with paint shop engineers to understand these high concentrations. Two reasons were found to be the cause for these high values. Firstly, as explained in the previous section, it was known that the ducts and exhaust systems of these areas might be interconnected with those of other areas and leaks of formaldehyde or other VOCs are possible. This is confirmed by the high formaldehyde concentrations observed. The second reason is related to accumulations of paint rests and sludge in the exhaust areas of the paint shop. This causes the slow release of solvents through the chimneys in higher concentrations than expected by the materials used in PVC and cavity wax applications.

The concentrations in the spray booth waste gas were low and comparable to the values observed in the other paint shops (0.47 mg/m^3). Regarding the ovens, like in the other paint shops, the values before their treatment in the abatement systems were high (4.51 and 3.41 mg/m^3 in electrocoating, 7.69 and 5.09 mg/m^3 in primer, 4.0 mg/m^3 in topcoat). However, in this case also high values were obtained after the abatement systems in electrocoating and topcoat. A further evaluation of the abatement installations was necessary to understand these results.

In the electrocoating oven, two recuperative thermal oxidizers were installed. An inspection of these installations allowed to understand the high formaldehyde concentration values observed. These abatement systems were at the end of their lifetime and leaks between the raw and the clean gas were identified. These leaks cause the waste gas from the oven loaded with solvents and formaldehyde to mix with the clean gas at the end of the system. As a result, even though the operating temperature of the system was correct, the abatement efficiency was not as designed, and formaldehyde was emitted at higher levels than expected. A repair or exchange of the recuperative thermal oxidizers is necessary to achieve the required destruction efficiency.

Regarding the high emissions at the exit of the abatement system for the topcoat oven, similarly to the electrocoating, an inspection of the equipment was carried out. In this process, an RTO operating at 840 ºC is installed. The inspection of this equipment concluded that the ceramic saddles used in the RTO chambers were contaminated with silicon dioxide, a co-product of the oxidation process. The abatement efficiency of the RTO was decreased and thus the formaldehyde emissions from the oven could not be reduced to lower levels. An exchange of the ceramic medium of the RTO is necessary to restore the original design efficiency.

2.4.6 Paint shop 6

Table 16 shows the results obtained in paint shop 6.

Table 16. Measurement results for paint shop 6.

Process related	Abatement Temperature °C	Average Formaldehyde concentration mg/m^3	Measurement uncertainty mg/m^3
Electrocoating abatement treated waste gas	810-815	0.024	0.001
Primer spray booth	N/A	0.094	0.006
Primer abatement treated waste gas	815	0.024	0.001
Topcoat spray booth	N/A	0.187	0.011
Topcoat flash off	N/A	0.058	0.004
Topcoat abatement treated waste gas	720	0.024	0.001
Spray booth special vehicles painting	N/A	0.047	0.003
Oven special vehicles painting exit after abatement	760	0.024	0.001

In this paint shop, only the direct emissions at the chimneys without any intermediate points were measured. The results obtained in the previous paint shops were confirmed. The spray booth values are low with a concentration of 0.187 mg/m^3. Moreover, the emissions after treatment in two RTOs for the electrocoating and primer ovens and in a recuperative thermal oxidizer for the topcoat oven were significantly low (values below the limit of detection of the measuring methodology, i.e., 0.024 mg/m^3), indicating that the abatement systems were properly functioning.

2.5 INVENTORY OF FORMALDEHYDE EMISSIONS FOR LCA

The emission results indicate that significant amounts of formaldehyde are emitted into the atmosphere if the drying ovens are functioning without air emissions abatement equipment or if the equipment is not properly operating. This might be caused by a low temperature in the oxidation process or if the equipment is damaged or requires a retrofit or exchange. Based on this information, paint shops 3 and 5 are the most affected.

Paint shop 3 had an insufficient operating temperature of 540 ºC in the primer oven abatement systems and the waste gas from the topcoat ovens was not treated. Besides, high concentrations of formaldehyde were found at the primer flash off waste gas. Regarding the paint shop 5 abatement systems, they were not operating at the design destruction efficiencies due to their age and damaged parts.

Considering that paint shop 3 operated their topcoat ovens without abatement equipment and the options to reduce formaldehyde emissions needed to be evaluated, this paint shop was selected for the LCA and the eco-efficiency analysis, as described in chapters 3 and 4. The measurements performed in this paint shop were directly used to compile the formaldehyde emissions data necessary to elaborate the Life Cycle Inventory (LCI) for the LCA. The elaboration of the LCI is further explained in chapter 3.

Table 17 shows the formaldehyde emissions data as used in the LCA. The measurement reports created by the measuring companies provided not only the concentration values at each emission source but also the mass flows emitted to the atmosphere in kilograms per hour. These data could be directly taken for the inventory. In some cases, not all emission points for one process or installation were measured to reduce the time and costs of the measurements, as explained in the methodology section. In such situations, the values obtained at the measured emission points were assumed to be the equal for the missing sources if the process was the same or the installation was operating at similar conditions. All mass flows from each source were finally summed up to obtain the total emissions of each process. Emissions sources from which formaldehyde emissions were not expected were neglected.

Table 17. Inventory of formaldehyde emissions for LCA.

Process related	Formaldehyde emission mass flow kg/h
Electrocoating baths, primer and topcoat booths	0.19
Electrocoating oven abatement systems	0.01
Primer flash off	0.17
Primer oven abatement systems	0.38
Basecoat spray booth clean air after VOC concentration system	0.08
Basecoat spray booth abatement system	0.12
Topcoat flash off	0.21
Topcoat ovens	0.89

2.6 CONCLUSIONS

In this chapter, the formaldehyde emissions measurements carried out at the six paint shops of the company were explained. This allowed to identify the processes and conditions under which formaldehyde is emitted at levels that exceed the legally applicable emission limit value, and collect first proposals to reduce the formaldehyde concentrations at the affected processes.

The hypothesis stated in chapter 1 was validated and confirmed for the first time in the company. In all paint shops, the concentrations of formaldehyde observed at the spray booths waste gas are insignificant and do not require further consideration. Concerning the drying ovens, the measured values after the oven before the waste gas enters the abatement system are high, confirming that formaldehyde is released in the ovens due to the use of melamine resins in the paints. Furthermore, only when the abatement equipment is working at temperatures higher than 700 ºC and there is no damage in the equipment that causes a reduction of the abatement efficiency, formaldehyde concentrations can be reduced to levels that ensure legal compliance.

The following list consolidates the main results of this chapter as well as a proposal for actions to reduce formaldehyde at the affected paint shops.

- Formaldehyde concentrations at the waste gas from spray booths are typically below 0.5 mg/m^3. These values are well below the applicable emission limit value of 2 mg/m^3 and demonstrate that the emissions from spray booths are not a concern from the legal perspective.
- The concentrations observed at the exit of the drying ovens, in particular for paint shops 2, 3, 4 and 5 confirm that formaldehyde is released in the ovens. The values vary from 2.13 mg/m^3 to 88.3 mg/m^3, depending on the paint shop. These fluctuations are reasonable since the operating conditions, e.g., temperature of the oven, number of vehicles being processed and paints used change from plant to plant and are also not constant in one individual plant.
- The high concentrations of formaldehyde after the oven can be successfully reduced to levels below the applicable emission limit value if the abatement equipment is operating at its design abatement efficiency. The concentrations after abatement were typically below 1 mg/m^3. In this regard, both RTO and recuperative thermal oxidizers are able to reduce formaldehyde achieving a similar result, as seen in paint shop 6.
- In paint shop 3, where recuperative thermal oxidizers were operating at 540 ºC, high concentration values close to 10 mg/m^3 were obtained. Formaldehyde concentrations after the abatement system operating at different temperatures were measured and the results indicate that the reduction of this substance to the required values can only be achieved at abatement temperatures higher than 700 ºC. As a consequence, the proposed action to reduce the emissions and ensure legal compliance is the increase of the abatement temperature to 730 ºC.
- The primer flash off waste gas in paint shop 3 contained formaldehyde in concentrations higher than the applicable emission limit value (3.4 mg/m^3). A proposed solution to reduce these emissions is to redirect the discharge of this waste gas into the primer abatement systems.
- The topcoat ovens in paint shop 3 were operated without abatement equipment. The results clearly demonstrate that the formaldehyde concentrations are higher than 10 mg/m^3 if the oven emissions are not abated. The proposed action for this paint shop is the installation of an abatement system for the topcoat ovens.
- In paint shop 5, even though the temperatures of the recuperative thermal oxidizers for the electrocoating and primer ovens and of the RTO for the topcoat oven seemed to be correct, the reduction of formaldehyde emissions was not achieved. An inspection of the

installations indicated that they had damaged or old parts that needed to be repaired or exchanged. The proposed actions for this paint shop consist of a complete exchange of the recuperative oxidizers for electrocoating and primer ovens as they reached the end of their lifetime and a removal and replace of the contaminated ceramic saddles in the RTO chambers. With this, a reduction of formaldehyde can be achieved.

- Even though melamine resins are not used in electrocoating, significant concentrations of formaldehyde were observed in paint shop 2 at the exit of the oven before the abatement system (10.4 mg/m^3). This result was attributed to formaldehyde residues that might be present in the materials used in the electrocoating baths and can be released during the curing process. Nevertheless, the electrocoating ovens were connected to recuperative thermal oxidizers that reduce formaldehyde to lower levels.
- Unexpectedly high concentrations of formaldehyde were observed at the waste gas from the PVC and wax application zones in paint shop 5 (2.15 and 2.66 mg/m^3). The results were mainly attributed to two reasons. Firstly, the ducts and exhaust systems of these areas might be interconnected with other zones of the painting processes and leaks of formaldehyde are possible. Secondly, accumulations of paint rests and sludge in the exhaust areas would cause a slow release of VOCs and formaldehyde through the chimney in higher concentrations than expected. A cleaning of these areas and a repetition of the measurements was proposed to the plant as actions to reduce the emissions and verify the effectiveness of this activity.

Considering all these results, it can be concluded that paint shop 3 is the most affected facility since the installation of a completely new abatement system for the topcoat ovens is necessary to reduce the formaldehyde emissions. This paint shop was selected for the LCA and eco-efficiency analysis as described in chapter 3 and 4. The measurement results obtained in this paint shop were used as input to elaborate the inventory for these assessments.

3 LIFE CYCLE ASSESSMENT

In chapter 2, the results of the formaldehyde measurements at the six paint shops of study as well as the actions proposed to reduce formaldehyde emissions were presented. In one of the six paint shops, high concentrations of formaldehyde were observed at the primer flash off, the waste gas from the primer abatement systems and the topcoat ovens operated without abatement.

Concerning the actions to reduce the emissions, several proposals were made for the different processes. Firstly, the primer flash off waste gas shall be treated in the primer oven abatement systems. Secondly, the temperature of the primer oven abatement systems must be increased to 730 ºC to achieve a proper abatement efficiency. Finally, an abatement system was proposed to be installed at the topcoat ovens to treat the formaldehyde released during the paint curing process. For this purpose, two different technologic options as described in chapter 1 shall be considered.

A Life Cycle Assessment (LCA) of the painting processes in this paint shop was performed from a “cradle-to-grave” perspective to analyze the environmental impacts before and after the introduction of the different improvement actions. With regard to the two topcoat oven abatement technologies evaluated, the LCA proved to be a reliable methodology to establish a comparison from the environmental sustainability point of view.

3.1 OBJECTIVES

The main objectives pursued in the Life Cycle Assessment are:

- Detect the hot spots from the main painting processes that cause the highest environmental impacts.
- Propose possible future actions to reduce the impacts based on the hot spots identified.
- Analyze the environmental impacts of the different actions that were already implemented in the paint shop to reduce formaldehyde emissions in order to compare the environmental situation before and after these actions.

This chapter partially reproduces content already published as “Granadero, D. [a,b], Garcia-Muñoz, A. [b], Adam, R. [b], Omil, F. [a] and Feijoo, G. [a], 2023. Evaluation of abatement options to reduce formaldehyde emissions in vehicle assembly paint shops using the Life Cycle methodology. Cleaner Environmental Systems, 11, 100139. ISSN 2666-7894, https://doi.org/10.1016/j.cesys.2023.100139.

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More information on the Publications section at the end of this Ph.D. thesis.

- Evaluate the change of the environmental impact of the painting process when introducing two different abatement systems for the reduction of formaldehyde emissions at the topcoat ovens, allowing the comparison of both technologies and supporting the selection of the most suitable system during the planning process.
- Introduce a potential future improvement action and evaluate the implications in terms of its environmental impacts.
- Perform a comparative analysis of all different scenarios of study from the total environmental impact and the human toxicity points of view to verify if the target of the Industrial Emissions Directive to protect the environment is achieved through these actions.

3.2 SCOPE

From the entire painting process electrocoating, primer and topcoat were evaluated as they are the most relevant sub-processes in terms of atmospheric emissions and, in particular, formaldehyde releases. The study considered only the operation of the equipment while the construction of the installations was left out of the LCA. The environmental impact of pre-treatment, sealing, waxing and repairing operations was considered not relevant and thus is not included in the scope of this work (VDI guideline 3455:2013-08).

3.2.1 Working conditions of the paint shop of study

The main working conditions of the paint shop studied are described below. A detailed scheme of the mass and energy balance of these three sub-processes can be seen in Appendix 1.

Electrocoating

The paint shop has two parallel baths with two ovens per bath, operating at a set temperature of 195 °C. Each oven has two recuperative thermal oxidizers to remove VOC emissions and unpleasant odors. These abatement systems are working at a temperature of 675 °C. The ovens and the abatement installations are fed with natural gas through burners. The heat excess of the recuperative oxidizers is used to heat the oven by means of heat exchangers.

Primer

For the primer application, the paint shop has a line with several spray booths in which a coating of waterborne primer is applied to the vehicle bodies using robots. This coating material is previously mixed with water to adjust the viscosity. The spray booth is followed by a flash off area before the ovens. The primer line has three ovens operating at 185 °C with three recuperative thermal oxidizers per oven running on natural gas. The total of nine abatement installations are operating at 540 °C. With the use of heat exchangers, the excess of heat from the abatement systems is provided to heat the ovens. In addition, there are several supporting burners heating the ovens apart from the heat recovered from the recuperative oxidizers.

Topcoat

The topcoat process is divided in the basecoat and clearcoat application, which are studied together. The two steps are separated by an intermediate flash off area. A second flash off zone is placed after the clearcoat application booths. Both basecoat and clearcoat paints are solvent borne and they are mixed with additional solvent before their application in order to reach the desired viscosity. Part of the VOCs contained in the waste gas from the basecoat spray booths are concentrated in an activated carbon unit (Berenjian et al., 2012) and further oxidized in one recuperative thermal oxidizer operating at 730 ºC. A second recuperative thermal oxidizer to increase the abatement capacity for the spray booth waste gas is installed but currently not in use.

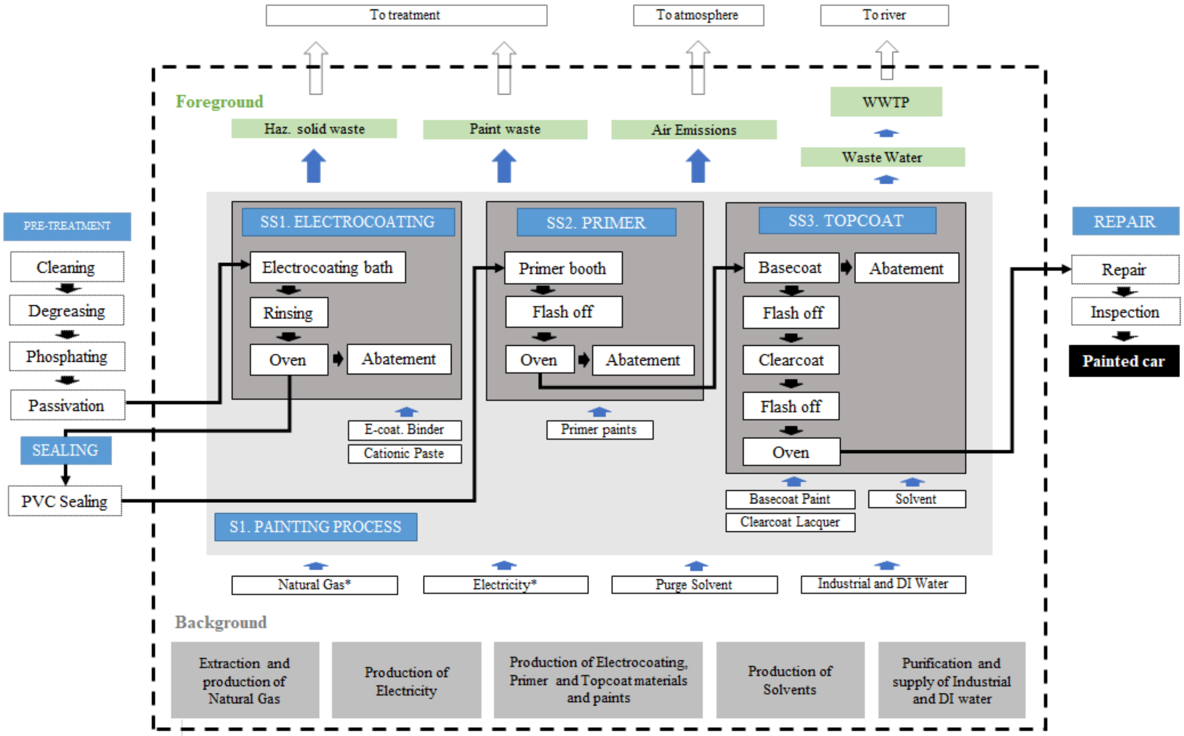
The topcoat process has four coating lines and two ovens at the end of each line, which makes a total of eight ovens running at 150 °C. The waste gas from the ovens is emitted to the atmosphere without abatement.

3.2.2 Functional unit

All the inputs and outputs of the painting process are related to the functional unit. The paint shop processes 360,000 vehicles per year, which corresponds to about 75 % of its total capacity. The functional unit selected was 1 hour of operation for each sub-process investigated.

3.2.3 System Boundaries

The system boundaries of this study are shown in Figure 12. Additionally, the figure illustrates the inputs and outputs to the sub-processes within scope as well as their background and foreground systems, used as the basis to elaborate the Life Cycle Inventory (LCI).



* Total painting processes consumption was split to the three subsystems based on allocation factors

Figure 12. Scheme of the system boundaries and background and foreground processes for the paint shop under evaluation.

As inputs to the painting operations natural gas, electricity, purge solvents, water and electrocoating and painting materials were considered. The background processes are those related to the production and supply of materials and energy necessary to operate the installations:

- *Extraction and production of Natural Gas*: Natural gas is needed to run the burners in order to heat the ovens and to operate the abatement equipment. It is provided by the natural gas supplier of the manufacturing plant. Its extraction and production processes cause environmental impacts, such as emissions to air, water depletion and wastewater generation (Shamoon et al., 2022).
- *Production of electricity*: Electricity is necessary to operate the paint shop installations, such as robots, air supply for spray booths, compressed air and lighting. The contribution of each energy source for the electricity generation was taken from the country mix where the paint shop is located.
- *Production of Electrocoating, Primer and Topcoat materials and paints*: The production of the various materials and paints used in the painting processes conforms a significant background process to this system. It implies raw material extraction, the use of energy and water for the production process, direct emissions, wastewater and waste generation (da Silva et al., 2016; Nair K et al., 2021; Shi et al., 2023).
- *Production of Solvents*: Similar to the production of materials and paints, the manufacturing of solvents used for viscosity adjustment of the paints as well as for cleaning of painting equipment has associated environmental impacts.
- *Purification and supply of industrial and DI (deionized) water*: Industrial and deionized water is used to carry out the electrocoating process and to wash out the overspray from the spray booths. Water coming from the river is processed and purified to be used in the paint shop in a series of decantation, decarbonization and filtration processes and, in the case of deionized water, a deionization process. The deionization is performed in an ion-exchange resin system.

As outputs from the painting operations the study reflects air emissions, waste and wastewater, whereof wastewater is treated onsite in a WWTP before discharge. In more detail, the foreground processes are:

- Emissions into the atmosphere of VOC, dust and formaldehyde from paint booths, ovens and air emissions abatement equipment and CO, CO_2 and NOx from burners and abatement equipment.
- Release of wastewater pollutants in concentrations below given thresholds, i.e. COD, TOC, Zinc, Iron, Phosphorus, Oil & greases, suspended solids and Fluorides, after the treatment in an onsite WWTP discharged into the river. Wastewater treatment is included in the system boundaries of this work.
- The generation of hazardous solid waste and other paint waste which leave the site to be treated in an off-site waste treatment facility. Waste treatment is outside of the system boundaries of this study.

3.3 DESCRIPTION OF SCENARIOS

As described in chapter 2, several actions were proposed to reduce formaldehyde emissions. Some actions were immediately implemented by the company while others were further assessed due to their complexity in implementation and the associated costs. Each action introduces a modification in the operational conditions of the painting processes, which ultimately leads to a change in the environmental impacts of the paint shop. In order to compare the environmental impact associated with each action, different scenarios were defined and analyzed. In this section, the various scenarios and the chronology of implementation of each of them are explained.

3.3.1 Chronology

Figure 13 shows the implementation timeline of the different scenarios studied in this work for the paint shop of study.

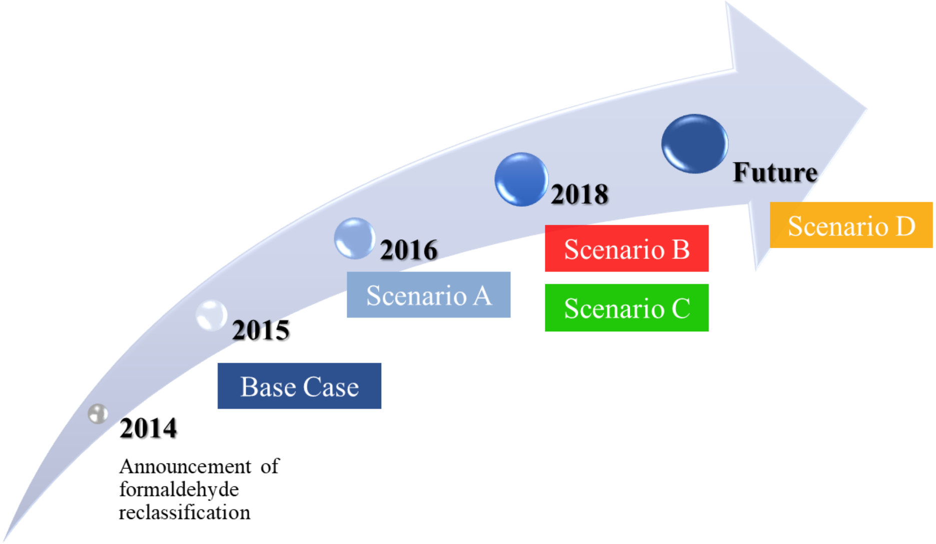


Figure 13. Implementation timeline of the different improvement scenarios. Each scenario corresponds to one or several actions to reduce formaldehyde emissions.

The initial scenario was defined as "Base Case" and represents the paint shop as it was operating in 2015 before any action was taken to reduce formaldehyde emissions. In 2016, the first set of actions was implemented, and this was included in "Scenario A". This consists of a reduction of the amount of free formaldehyde in the paints carried out by paint manufacturers and a decrease of the emissions from the primer process by introducing technical and operational improvements.

In 2018, the company efforts were focused on reducing the emissions from the topcoat ovens. For this purpose, two alternative technologies were considered. "Scenario B" represents the installation of an RTO whereas "Scenario C" includes the installation of several recuperative thermal oxidizers. In addition, a potential future improvement scenario for the basecoat spray booth waste gas was analyzed as "Scenario D". The different scenarios are described in more detail below.

It is important to highlight that only the environmental impacts caused by the painting process working under these modifications were analyzed and not the impact of the implementation itself.

3.3.2 Scenario A

The first scenario includes different actions immediately implemented in the paint shop when high levels of formaldehyde were identified through the measurements at the relevant chimneys. As explained in chapter 1, paint manufacturers improved their production processes to reduce the amounts of free formaldehyde in their paints due to the new hazardous classification of formaldehyde. In Scenario A, a reduction of the free formaldehyde concentration in the composition of the primer and topcoat paints from 0.3 % (weight) in the

Base Case to 0.099 % was considered. The latter value corresponds to the maximum concentration possible (worst case) that the paints may have to avoid the disclosure of formaldehyde in the MSDS.

As discussed in chapter 2, high concentrations of formaldehyde were detected in the primer flash off waste gas. The second action considered in Scenario A was the redirection of this waste gas stream to the primer ovens and thus ensure its treatment in the primer oven abatement systems.

Furthermore, the abatement installations for the primer ovens were initially operating at 540 °C. The temperature of the primer oven abatement installations was raised to 730 °C. The increase of the natural gas consumption as well as the changes in the emissions of CO, VOCs, formaldehyde and NOx due to the modification of the temperature were included in Scenario A.

3.3.3 Scenarios B and C

High concentrations of formaldehyde were also detected in the waste gas from the ovens placed at the end of the topcoat process. To reduce the emissions, two alternative treatment methods corresponding to the two different abatement technologies described in chapter 1 were considered. Each technology corresponds to one scenario.

As part of this work, the number of installations for each type of technology necessary to treat the total waste gas volumes from the ovens was estimated. In addition, an evaluation of the energy demanded for each type of installation was performed.

Scenario B

Scenario B considers the installation of a 5-bed RTO for the topcoat ovens. The energy necessary for this installation is supplied by three burners with a nominal power of 0.9 MW each using natural gas as fuel. An abatement efficiency of 100 % was assumed for this system.

Scenario C

For Scenario C, eight recuperative thermal oxidizers are assumed to treat the waste gas volume from the topcoat ovens. To provide energy to the oxidizers, it is necessary to install one burner per oxidizer with a nominal power of 1.25 MWh using natural gas. The excess heat of the clean gases is used to heat the ovens, leading to an overall energy saving in the plant since the existing burners to heat the ovens would be shut down and removed. An abatement efficiency of 99 % was assumed for recuperative oxidizers.

3.3.4 Future improvement Scenario D

In addition to the installation of an air emissions abatement system for the topcoat ovens, other future improvements were analyzed to reduce VOC and formaldehyde emissions. Currently, the plant has two recuperative thermal oxidizers installed for the treatment of the basecoat spray booths waste gas. To save energy, one of the two installations was switched off and thus only 50 % of the basecoat spray booth emissions are being treated.

In Scenario D, the painting process with a complete treatment of the emissions from the basecoat spray booths was analyzed, that is, both oxidizers operating at its whole capacity. This scenario was simulated taking as a basis the data of Scenario B.

3.4 METHODOLOGY

An attributional LCA of the painting process in the paint shop studied was performed from a "cradle-to-grave" perspective following the requirements and guidelines of the ISO 14040:2006 and ISO 14044:2006.

3.4.1 Impact assessment

A Life Cycle Impact Assessment (LCIA) was conducted using commercial software SimaPro v.8.2 with European ReCiPe Midpoint V1.12 methodology, using the EcoInvent v3.2 database. This method is scientifically sound, easy to use and interpret, and internationally accepted. The method focuses on environmental impact and damage, distinguishing 18 different impact categories (Geldermann and Rentz, 2005; ILCD, 2010 a; ILCD, 2010 b; Goedkoop et al., 2013).

The impact assessment is a technical, quantitative and qualitative process to characterize and measure the effects of the environmental burdens identified in the Life Cycle Inventory (LCI). This approach allows the identification of the elementary flows of the LCI that have a relevant effect to different environmental and human health impact categories.

The following impact categories are considered within the selected methodology:

- *Climatic change* (CC) (kg CO_2 eq.): Impact related to the average increase of temperature of the terrestrial atmosphere and of the oceans observed in the last decades. The midpoint level uses the latest (2007) IPCC equivalency factors for three-time horizons (20, 100 and 500 years).
- *Ozone layer depletion* (OD) (kg CFC-11 eq.): It measures the negative effects on the ability to protect against ultraviolet radiation from the atmospheric ozone layer. Based on time-explicit forecast of demographic developments up to 2100.
- *Terrestrial acidification* (TA) (kg SO_2 eq.): Linked to Ecosystem damage and time horizon dependent. It analyzes the decrease on the neutralizing capacity of soil.
- *Fresh water eutrophication* (FE) (kg P eq.) and *Marine eutrophication* (ME) (kg N eq.): Excessive growth of the algae population due to the artificial enrichment of river, reservoir or marine waters as a result of the massive use of fertilizers and detergents.
- *Human toxicity* (HT) (kg 1.4-DB eq.): It considers the harmful effects on human health due to the absorption of toxic substances through inhalation of air, food or water intake, or penetration through the skin.
- *Photochemical oxidant formation* (POF) (kg NMVOC): Photochemical pollution occurs due to the presence of oxidants, caused by the reaction of nitrogen oxides, hydrocarbons and oxygen with ultraviolet radiation from the sun. It is the principal responsible of tropospheric ozone which is hazardous for the human health.
- *Particular matter formation* (PMF) (kg PM10 eq.). Particles and inorganic substances with respiratory effects. It measures the harmful effects on human health due to particulate emissions and their precursors (NOx, SOx, and NH_3).
- *Terrestrial ecotoxicity* (TET), *Fresh water ecotoxicity* (FET) and *Marine ecotoxicity* (MET) (kg 1.4-DB eq.): Ecotoxicity is the result of a number of different toxicological mechanisms caused by the release of substances with a direct effect on the health of the ecosystem. These categories of environmental impact are related to the toxic impacts

that affect to terrestrial, fresh water or marine ecosystems, that are harmful to different species and that change the structure and function of the ecosystem.

- *Ionizing radiation* (IR) (kBq U235 eq.): Related to the damage to Human Health due to the radioactive material emissions to the environment.
- *Agricultural Land Occupation* (ALO) and *Urban Land Occupation* (ULO) (m^2a): Category of impact related to the use (occupation) and conversion (transformation) of an area of land by agricultural or urban activities.
- *Natural Land Transformation* (NLT) (m^2): Related to the change from one land use category to another. For example, plantation of forest on land previously used for agriculture.
- *Water depletion* (WD) (m^3), *Metal depletion* (MD) (kg Fe eq.) and *Fossil depletion* (FD) (kg oil eq.): Related to the consumption of material extracted directly from the environment.

After the selection of the impact categories and the classification of the inventory results as the initial steps of the impact assessment, the characterization and normalization steps defined in the ISO 14040 and ISO 14044 standards were followed.

3.4.1.1 Characterization

The ISO 14040 standard on Life Cycle Assessment determines the characterization as mandatory. The impact of each emission or resource consumption is modelled quantitatively with the use of characterization factors.

The characterization of the painting process in its initial situation (Base Case) was performed to identify the sub-process with the greatest environmental impact. In addition, a characterization of each individual sub-process (electrocoating, primer and topcoat) was conducted to obtain the inputs and outputs with the highest contribution to the environmental impact. The next step was the characterization of the system for the Scenarios A, B and C, and finally Scenario D.

3.4.1.2 Normalization

Although the ISO 14040 standard does not indicate the normalization as mandatory, it is useful to better compare the environmental impact of the painting process in the different analyzed scenarios. In this step, the results of the characterization step are normalized by expressing them with respect to a chosen reference system.

For the comparison of the normalized data, in a first analysis, all 18 impact categories included in the methodology were taken into account. In subsequent stages, the most relevant impact categories were selected on the basis of these two criteria:

- All impact categories whose relevant contribution to the total environmental impact was higher than 2 %. Eight categories could be identified by evaluating the normalization results. These eight relevant impact categories contribute to 95.5 % to the total environmental impact.
- Human toxicity (HT) exclusively, since the reduction of human toxicity through the reduction of formaldehyde emissions due to its cancer-causing characteristic is the objective of the actions included in the different scenarios in this study.

3.5 LIFE CYCLE INVENTORY

Life Cycle Inventory (LCI) is a compilation and quantification of input and output data with regard to the studied system. The outcome of the LCI catalogues the flows crossing the system boundary and provides the starting point for Life Cycle Impact Assessment (LCIA) (ISO 14040:2006; ISO 14044:2006).

3.5.1 System definition and data quality

Figure 14 shows the steps followed for the development of this study. The section marked in green color illustrates the system definition, i.e., the basic bibliographic and technical information required to understand the company, the painting process and the problem of study. The section in blue refers to the data quality process steps.

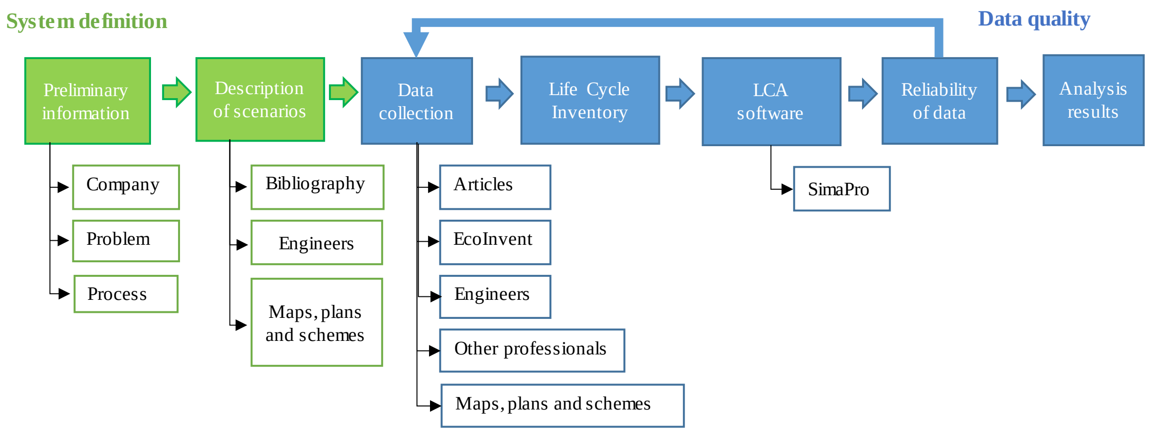


Figure 14. System definition and data quality.

Once all the preliminary required information was collected, a qualification of all inputs and outputs of the system was carried out and different diagrams and mass and energy balances were elaborated (Appendix 1). As a next step, the quantification of the data was performed to elaborate the inventory. For this purpose, several types of sources were consulted to obtain reliable and accurate data.

When all data were complete, the inventory was transferred to the software SimaPro for the LCIA. It must be highlighted that some iterations in the software were needed to achieve the highest accuracy possible. These iterations are illustrated in Figure 14.

3.5.2 Types and sources of data

Data selected for a LCIA depends on the goal and scope of the study. For the development of this work, most of the data were collected from the paint shop of study. Besides, other data from alternative sources such as books or publications, other similar plants, internal communications, or additional information were needed to complete all missing data and elaborate the inventory. All data collected in this work include a combination of measured, calculated and estimated values. In this chapter, all inventories are shown indicating the source of each value and, when required, how it was calculated.

Data were classified according to their level of reliability:

1. *Data from the paint shop*. As far as possible, real data from the studied paint shop were used. A number of reports with measurements results and meter readings data were reviewed for this purpose. All the data compiled for the inventories of the Base Case scenario were from 2015.
2. *VOC and material balances from the plant*. To obtain the total VOC emissions from the painting process for the Base Case and the different scenarios, a VOC mass balance calculation template was developed and provided to the plant engineers to fill in with the necessary input data. The calculation methodology is based on the principles and definitions prescribed in the Industrial Emissions Directive 2010/75/EU and the STS BREF, 2020. The methodology as well as the results of the calculations for the different scenarios can be seen in Appendix 2.
3. *Safety Data Sheets* (Regulation (EC) No 1907/2006) of the paints and other materials used (REACH) and additional information from the material suppliers. In the case of this additional information, it was provided by external companies.
4. *Calculations based on data given by the plant*. Assumptions and calculations were made to allocate some of the data provided by the plant engineers on material and energy consumption.
5. *Internal communications*. Specific information required to elaborate the inventory was not available in any report from the plant. In these cases, workshops were conducted with paint shop engineers and experts in the paints, the processes and water and energy management, to collect the necessary data. The information from this source was considered reliable and could be considered for the purpose of this work.
6. *Data from a different plant* of the same company with similar processes and equipment. Some data were not available from the studied paint shop, therefore reports from similar plants of the company were taken.
7. *Bibliographic information*. Books, publications, legislation and BREF documents were reviewed to understand the common vehicle painting processes and to verify and allocate the data to the studied processes.
8. *Other calculations*. It is referred to estimations made through different sources or following simple mathematical rules.

Most of the data were compared between different sources to ensure its veracity, especially when these data were obtained as a percentage or a range value.

3.5.3 Inventory

The LCI data presented in this section correspond to the stepwise painting process in the Base Case scenario. Data were collected for one year of production and all data refer to the functional unit of 1 hour of operation. Even though the reduction of formaldehyde emissions constitutes the focus of this work, the emissions of all other air and water pollutants that occur in the vehicle paint shop were considered to elaborate the life cycle inventories.

3.5.3.1 Electrocoating process

The first sub-system entered in the software SimaPro was the electrocoating process. Table 18 shows the inventory for this process.

Table18. LCI for the electrocoating process.

	SS1: Electrocoating	Unit	Method / Source of data
INPUTS: from Technosphere			
Materials			
Water DI	2.39	m^3	Paint shop consumption records [1, 5]
Binder:			Paint shop consumption records [1]
Organic solvent	12.18	kg	MSDS [3]
Epoxy resins	203	kg	Supplier information [5]
Water	190.82	kg	Calculation [8]
Cationic paste:			Paint shop consumption records [1, 5]
Organic Solvent	139.09	kg	MSDS [3]
Epoxy resins	794.8	kg	Supplier information [5]
Pigment	397.4	kg	Supplier information [5]
Water	655.71	kg	Calculation [8]
Energy			
Natural Gas	4.81	MWh	Paint shop energy records [1]
Electricity	2.04	MWh	Paint shop energy records [1]
Cogeneration	1.38	MWh	Paint shop energy records [1, 6, 7]
OUTPUTS: emissions to the environment			
Emissions to air			
Dust	0.05	kg	Measured, Calculated [1, 4]
NOx	4.15	kg	Measured, Calculated [1, 4]
CO	20.6	kg	Measured, Calculated [1, 4]
CO_2	1193	kg	Measured, Calculated [1, 4]
VOCs	4.42	kg	Calculated [2]
Formaldehyde	0.01	kg	Measured, Calculated [1, 4]
Emissions to water			
COD	222	g O_2	Measured, Calculated [1, 4]
TOC	59.8	g	Measured, Calculated [1, 4]
Zinc	1.7	g	Measured, Calculated [1, 4]
Iron	2.4	g	Measured, Calculated [1, 4]
Phosphorus	6.86	g	Measured, Calculated [1, 4]
Oil & greases	7.45	g	Measured, Calculated [1, 4]
Suspended solids	41	g	Measured, Calculated [1, 4]
Fluorides	15.8	g	Measured, Calculated [1, 4]

[1] Data from the plant: reports, measurements.
[2] VOC and material balances from the plant.
[3] Safety Data Sheets from the materials (REACH).
[4] Calculations based on data given by the plant. Assumptions were made in order to obtain the allocation of some data.
[5] Internal communications from the plant or suppliers.
[6] Data from a different plant of the same company with similar processes and equipment.
[7] Bibliographic information from legislation, publications or books, allocation following BREF documents or provided from country specifications.
[8] Other calculations

Paint materials

Cationic paste and binder materials were included in the SimaPro software as sub-systems. Therefore, the information of the materials composition provided by the electrocoating process experts was necessary, as well as the safety data sheets of the paints and material reports.

Natural gas consumption

The total amount of natural gas used in the whole paint shop, including the processes out of the system boundaries was available. A calculation was made to estimate the real consumption for each sub-process within the system boundaries. The calculation is detailed in the Appendix 3.

Electricity **Section affected by copyright protection.**

Following the Surface Treatment using Organic Solvents BREF document (STS BREF, 2020), the allocation to the different processes within the system boundaries was made using the average percentages indicated in this document. The contribution of each energy source for the electricity generation was taken from the country where the plant is located. The same procedure was applied for primer and topcoat processes.

Air emissions

All air emissions data were collected from real measurements at the different areas of the process, i.e., the spray booths, flash off areas and oven abatement systems. The inventory values were calculated as the sum of the emission loads measured at all emission sources of the different sub-processes of the paint shop. The measurement uncertainties of the method are as follows: Dust: n. a.; NOx: 15 %; CO: 9 %; Formaldehyde: 15 %. As indicated above, VOC emissions were calculated through the annual VOC mass balance calculation template.

Water emissions

A report from the plant with wastewater measurements was used containing the emissions in oily and chemical wastewater streams. The inventory values were calculated by means of the annual average concentration values for these two different wastewater streams and considering the total volume flows and operating hours.

3.5.3.2 Primer process

Similar to the electrocoating process, the LCI for the primer process can be seen in Table 19.

Table 19. LCI for primer process.

	SS2: Primer	**Unit**	**Method / Source of data**
INPUTS: from Technosphere			
Materials			
Primer Paints:			Paint shop consumption records [1]
Organic solvent	4.82	kg	MSDS [3]
Polyester resins	15.41	kg	Bibliographic research [7, 8]
Amino resins	6.74	kg	Supplier information [5]
Free formaldehyde	0.1	kg	Supplier information [5]
Polyurethane	1.93	kg	Bibliographic research [7, 8]
Water	38.52	kg	Calculated [4, 8]
Pigments	28.89	kg	Calculated [4, 8]
Energy			
Natural Gas	6.23	MWh	Paint shop energy records [1]
Electricity	2.35	MWh	Paint shop energy records [1]
Cogeneration	1.59	MWh	Paint shop energy records [1, 6, 7]
OUTPUTS: emissions to the environment			
Emissions to air			
Dust	0.27	kg	Measured, Calculated [1, 4]
NOx	8.09	kg	Measured, Calculated [1, 4]
CO	2	kg	Measured, Calculated [1, 4]
CO_2	n.a.	kg	
VOCs	1.3	kg	Calculated [2]
Formaldehyde	0.01	kg	Measured, Calculated [1, 4]

[1] Data from the plant: reports, measurements.
[2] VOC and material balances from the plant.
[3] Safety Data Sheets from the materials (REACH).
[4] Calculations based on data given by the plant. Assumptions were made in order to obtain the allocation of some data.
[5] Internal communications from the plant or suppliers.
[6] Data from a different plant of the same company with similar processes and equipment.
[7] Bibliographic information from legislation, publications or books, allocation following BREF documents or provided from country specifications.
[8] Other calculations

Paint materials

Four different primer materials were found in the reports from the plant. As all these materials have similar composition, all of them were included as a unique primer paint. This paint was added to the process as a sub-system created by data obtained from different sources. Percentages of organic solvent, amino resin and free formaldehyde from the paint were taken from the plant. The ratio amino-polyester resin of the total resin present in common vehicle´s paint is 30:70. This ratio is based on a bibliographic reference (Stoye D., 1993). Information of the total resin (including amino, polyester and polyurethane) was given by the paint department so that it was possible to estimate the amount of polyester in its composition. Finally, water and pigment percentages were also provided by the experts of this process.

Natural Gas consumption, electricity and air emissions

These values were obtained following the same procedure as in the previous process. CO_2 emissions were not measured in the primer process and therefore it was catalogued as not available data.

Water emissions

Allocation of wastewater for this process was not possible to establish.

3.5.3.3 Topcoat process

The last process analyzed was the topcoat that includes basecoat and clearcoat application. The LCI data from these two steps are detailed in the Table 20.

Table 20. LCI for the topcoat process.

	SS3: Topcoat	**Unit**	**Method / Source of data**
INPUTS: from Technosphere			
Materials			
Basecoat Paints:			Paint shop consumption records [1]
Organic solvent	85.4	kg	MSDS [3]
Polyester resins	32.2	kg	Bibliographic research [7, 8]
Amino resins	14	kg	Supplier information [5]
Free formaldehyde	0.14	kg	Supplier information [5]
Pigment white	0.14	kg	Calculated [4, 8]
Pigment Black/grey	4.2	kg	Calculated [4, 8]
Pigment Blue/Green	0.84	kg	Calculated [4, 8]
Additives	1.4	kg	Supplier information [5]
Basecoat White Paint:			Paint shop consumption records [1]
Organic Solvents	19.32	kg	MSDS [3]
Polyester Resins	7.14	kg	Supplier information [5]
Amino resins	2.94	kg	Supplier information [5]
Free formaldehyde	0.04	kg	Supplier information [5]
Pigment white	11.76	kg	Supplier information [5]
Additives	0.84	kg	Supplier information [5]
Clearcoat Lacquer:			Paint shop consumption records [1]
Organic solvent	82.81	kg	MSDS [3]
Amino resins	28.73	kg	Supplier information [5]
Hydroxyl Resin / Acrylic	52.39	kg	Supplier information [5]
Free formaldehyde	0.17	kg	Supplier information [5]
Additives	5.07	kg	Supplier information [5]
Solvents Basecoat (viscosity adjustment):			Paint shop consumption records [1]
Butanol	7.28	kg	MSDS [3]
Butylacetate	25.48	kg	MSDS [3]
Xylene	53.69	kg	MSDS [3]
Solvent organic	5.46	kg	MSDS [3]

Energy			
Natural Gas	15.2	MWh	Paint shop energy records [1]
Electricity	7.22		Paint shop energy records [1]
Cogeneration	4.88	MWh	Paint shop energy records [1, 6, 7]
OUTPUTS: emissions to the environment			
Emissions to air			
Dust	10.71	kg	Measured, Calculated [1, 4]
NOx	35.02	kg	Measured, Calculated [1, 4]
CO	4.3	kg	Measured, Calculated [1, 4]
CO_2	n.a.	kg	
VOCs	200.57	kg	Calculated [2]
Formaldehyde	1.36	kg	Measured, Calculated [1, 4]

[1] Data from the plant: reports, measurements.
[2] VOC and material balances from the plant.
[3] Safety Data Sheets from the materials (REACH).
[4] Calculations based on data given by the plant. Assumptions were made in order to obtain the allocation of some data.
[5] Internal communications from the plant or suppliers.
[6] Data from a different plant of the same company with similar processes and equipment.
[7] Bibliographic information from legislation, publications or books, allocation following BREF documents or provided from country specifications.
[8] Other calculations

Paint materials

In 2015, 31 different paints for basecoat and one paint lacquer for clearcoat were used from three distinct suppliers. All MSDS of the paints were analyzed. Since these paints have similar composition except the paint used for white coating, two kinds of paints were included as subsystems with some variations in its composition. The subsystem called “Basecoat White” is associated to this specific white color paint, whose composition was provided by the paint supplier. The other subsystem, “Basecoat paint” includes the rest of the paints.

Solvent

All paints used in topcoat application were solvent-based. To achieve the necessary viscosity of the paints, they are mixed with two different solvents. The solvent included in the system combines the composition of both solvents specified in the MSDS for each one.

Natural gas consumption, electricity and air emissions

These values were obtained following the same procedure as in the previous process. CO_2 emissions were not measured at the topcoat process so it was catalogued as not available data.

Water emissions

Allocation of wastewater for this process was not possible to establish.

Missing data

The percentage of additives included in the paints were known. However, additives are referred to a mixture of several compounds that was not possible to determine to be introduced in the system. As this amount is below 5 % of the total composition, it was left out of the system in the paints.

3.5.3.4 Painting process

To analyze the three sub-processes together in the SimaPro software and to have a global view of the whole painting process within the system boundaries, the three subsystems were included in a global system called "Painting process". Moreover, all data that was not possible to separate and allocate in each process were added in this global system.

Table 21 contains the data for the painting process that could not be allocated to the three subsystems.

Table 21. LCI for the painting process.

	S1: Painting Process	Unit	Method / Source of data
INPUTS: from Technosphere			
Materials			
Water DI	8.39	m^3	Paint shop consumption records [1, 5]
Purge solvent	73.1	kg	Paint shop consumption records [1, 8]
Industrial water	16.07	m^3	Paint shop consumption records [1, 6, 8]
OUTPUTS: emissions to the environment			
Emissions to air			
Dust	3.51	kg	Measured, Calculated [1, 4]
NOx	24.62	kg	Measured, Calculated [1, 4]
CO	7.4	kg	Measured, Calculated [1, 4]
CO_2	433	kg	Measured, Calculated [1, 4]
VOCs	73.13	kg	Calculated [2]
Formaldehyde	0.12	kg	Measured, Calculated [1, 4]
Emissions to water			
COD	3.25	g O_2	Measured, Calculated [1, 4]
TOC	0.99	g	Measured, Calculated [1, 4]
Zinc	0.03	g	Measured, Calculated [1, 4]
Iron	0.03	g	Measured, Calculated [1, 4]
Phosphorus	0.11	g	Measured, Calculated [1, 4]
Oil & greases	0.11	g	Measured, Calculated [1, 4]
Suspended solids	0.59	g	Measured, Calculated [1, 4]
Fluorides	n.a.	g	
Waste			
Emulsion paints to incineration	4.37	kg	Paint shop waste records [1]
Paint to be separated	68.6	kg	Paint shop waste records [1]
Solid hazardous to incineration	1.78	kg	Paint shop waste records [1]

[1] Data from the plant: reports, measurements.
[2] VOC and material balances from the plant.
[3] Safety Data Sheets from the materials (REACH).
[4] Calculations based on data given by the plant. Assumptions were made in order to obtain the allocation of some data.
[5] Internal communications from the plant or suppliers.
[6] Data from a different plant of the same company with similar processes and equipment.
[7] Bibliographic information from legislation, publications or books, allocation following BREF documents or provided from country specifications.
[8] Other calculations

Water inputs

The amount of water in the reports is referred to the total water consumption for the whole plant. To estimate the water for the processes within the system boundaries, information from other plants of the company was consulted.

Purge solvent

The purge solvent is used to clean the application guns and equipment in the primer and topcoat booths. The consumption data of this solvent was obtained from reports provided by the plant. This solvent includes virgin and recycled material.

Emissions to air

These values include the measurements results from the chimneys that discharge the waste gas from electrocoating, primer and basecoat booths together, and no allocation to the individual processes was possible.

Emissions to water

Wastewater measurements results from the primer and topcoat processes after the WWTP were included.

Waste

All main waste streams related to the painting processes were included.

3.5.4 Inventory for the improvement scenarios

To analyze the impact of the different studied scenarios, several modifications in the inventories as explained above were required. Table 22 compiles the changes highlighting which process was affected.

Table 22. LCI modifications for the studied scenarios.

	Process affected	Base case	Scenario A	Scenario B	Scenario C	Scenario D	Unit	Source
Material modification								
Primer paint (free formal.)	Primer	0.30 %	0.099 %	0.099 %	0.099 %	0.099 %		Paint suppliers[3]
Base Coat paint (free formal.)	Topcoat	0.30 %	0.099 %	0.099 %	0.099 %	0.099 %		
Base Coat White paint (free formal.)	Topcoat	0.30 %	0.099 %	0.099 %	0.099 %	0.099 %		
Clear coat paint (free formal.)	Topcoat	0.30 %	0.099 %	0.099 %	0.099 %	0.099 %		
Energy modification								
Natural gas	Primer	6.23	7.77	7.77	7.77	7.77	MWh	Calculations*
Natural gas	Topcoat	15.2	15.2	17.9	12.7	19.0	MWh	Calculations*
Air emissions modification								
VOC	Primer	1.84	1.32	1.32	1.32	1.32	kg/h	VOC balance**
VOC	Topcoat	201	201	172	172	92.4	kg/h	VOC balance**
Formaldehyde	Primer	0.545	0.009	0.009	0.009	0.009	kg/h	Measurements 2015-2016[1]
Formaldehyde	Topcoat	1.36	1.36	0.475	0.475	0.285	kg/h	VOC balance**
NOx	Primer	3.32	8.09	8.09	8.09	8.09	kg/h	Measurements 2015-2016[1]
NOx	Topcoat	35.0	35.02	56.74	56.74	91.76	kg/h	Measurements other abatement 2015 [6]
CO	Primer	11.42	2.00	2.00	2.00	2.00	kg/h	Measurements 2015-2016[1]
CO	Topcoat	4.27	4.27	9.63	9.63	13.90	kg/h	Measurements other abatement 2015 [6]

* Calculations for the different scenarios are explained in Appendix 4.

** The specific VOC mass balance calculations considering the emission, transfer, abatement and waste factors for each scenario in each process are shown in Appendix 2.

[1] Data from the plant: reports, measurements.

[3] Safety Data Sheets from the materials (REACH).

[6] Data from a different plant of the same company with similar processes and equipment.

Paints

Scenario A contemplates a change in the composition of all the paints used at the plant. The amount of free formaldehyde in the paints was reduced to a value below 0.1 %. Thus, the higher amount possible was assumed (0.099 %). This value was considered for the next scenarios.

Natural Gas variation

The variation of the natural gas for the Scenario A was provided by the paint shop engineers. In Appendix 4, the necessary data used to calculate the variation for the Scenarios B and C is shown. Finally, for Scenario D the variation assumed was two times the current consumption of the basecoat spray booth abatement system.

VOC and formaldehyde

VOC emissions were calculated by applying the VOC mass balance template simulating the different characteristics for each improvement scenario. The mass balances and the calculations can be seen in Appendix 2. Formaldehyde emissions for the different scenarios were estimated starting from the results of the measurements carried out in the paint shop as explained in chapter 2 and considering the improvements introduced by the different scenarios.

NOx and CO

For the scenarios that were not implemented in the plant at the time this study was carried out, air emissions data related to the abatement installations (NOx and CO) were not available. Therefore, data from other plants of the company with similar processes and equipment were taken and adapted to the studied plant.

3.6 RESULTS AND DISCUSSION

The Life Cycle Impact Assessment is the phase of the LCA that involves the evaluation of the magnitude and significance of the potential environmental impacts of the system. The interpretation is the evaluation of the results in relation to the objectives and scope of the work in order to reach conclusions and recommendations for improvement (ISO 14040:2006; ISO 14044:2006).

Once all data were collected in the inventories described in the previous section and entered in the SimaPro software, the results were obtained and analyzed. This section presents the results of the characterization and normalization steps and provides an interpretation and discussion of the results in order to address the objectives described in chapter 3.1.

3.6.1 Characterization painting process Base Case

In the characterization step, the hot spots were detected by analyzing the contribution of the different subsystems to the impact categories. An initial assessment of the overall painting process (Figure 15), comprising the inputs and outputs of the electrocoating, primer and topcoat processes, as well as all other inputs and outputs that could not be assigned to the three subsystems, shows that the topcoat process has the largest contribution for most impact categories. The smallest effect of the topcoat process can be noticed in the WD impact category with 42.7 m^3 in a total of 248.8 m^3 (17.1 %), whilst the highest share of this process in an impact category can be observed in POF with 252.2 kg NMVOC in a total of 419.2 kg NMVOC (59.5 %). Furthermore, the impact categories MD = 252.1 kg Fe eq. for the topcoat process (a contribution of 61.0 % to the total of the impact category), FET = 165.6 kg 1,4-DB eq. (57.8 %), MET = 138.1 kg 1,4 DB eq. (57.8 %), NLT = 1.53 m^2 (57.3 %), OD = 0.001 kg CFC 11 eq. (55.8 %), ALO = 115.1 m^2a (56.0 %), TET = 0.68 kg 1,4 DB eq. (54.3 %) and IR = 242.0 kBq U235 eq. (55.4 %) are remarkably affected by the topcoat process as the given percentages indicate.

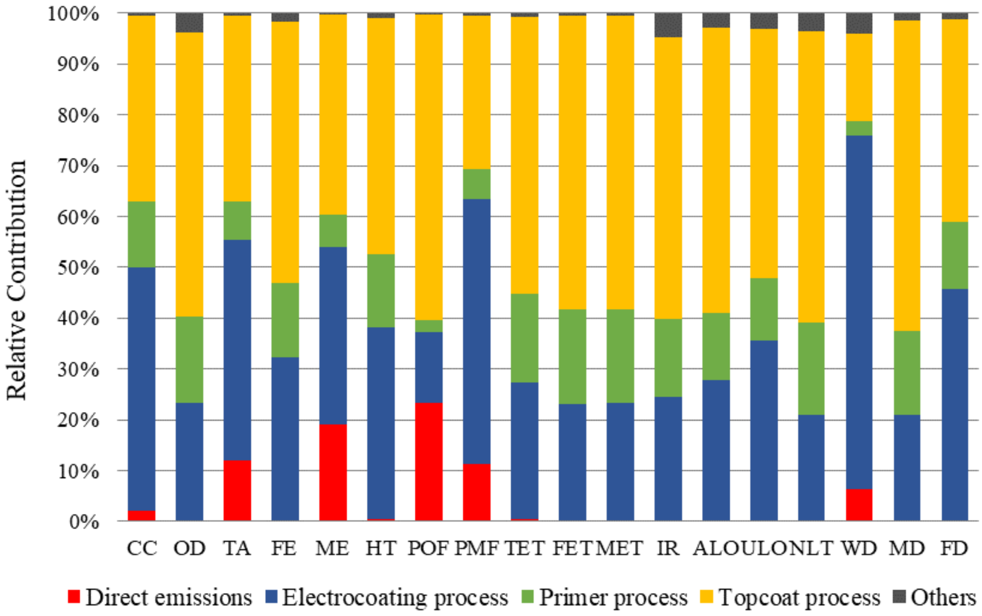


Figure 15. Results of the LCI characterization for the overall painting process in the Base Case (S1). Acronyms used in this figure: CC: Climate Change; OD: Ozone Depletion; TA: Terrestrial Acidification; FE: Freshwater Eutrophication; ME: Marine Eutrophication; HT: Human Toxicity; POF: Photochemical Oxidant Formation; PMF: Particulate Matter Formation; TET: Terrestrial Ecotoxicity; FET: Freshwater Ecotoxicity; MET: Marine Ecotoxicity; IR: Ionizing Radiation; ALO: Agricultural Land Occupation; ULO: Urban Land Occupation; NLT: Natural Land Transformation; WD: Water Depletion; MD: Metal Depletion; FD: Fossil Depletion.

These results can be explained by the fact that the topcoat is the process with the highest consumption of materials and producer of emissions, in particular the use of solvent-borne paints, higher consumption of natural gas due to the use of more burners to heat the drying ovens than in the other sub-processes, and the direct emissions into the atmosphere without installed abatement systems. A similar outcome was observed by Bianco et al., 2020, specifically for the POF impact category, who identified the provision of heating and the direct emissions of VOCs as hot spots of the vehicle painting process.

Additionally, it can also be observed that the electrocoating process plays an important role in all impact categories, with the greatest contribution in the categories of WD = 173.0 m^3 (69.5 % contribution to the total of the impact category), PMF = 25.2 kg PM10 eq. (52.1 %), CC = 10224.5 kg CO_2 eq (48.0 %), FD = 3587.1 kg oil eq. (45.9 %) and TA = 49.1 kg SO_2 eq. (43.2 %), primarily due to the materials used in this process. Subsequently, the three subsystems were analyzed separately.

3.6.1.1 Characterization electrocoating process Base Case

Figure 16 shows the results of the characterization of the electrocoating process. For most of the impact categories, the materials used in the electrocoating baths, i.e., the binder, consisting of organic solvents, epoxy resins and water, and the cationic paste, which is made of organic solvents, epoxy resins, pigments and water, make the greatest contribution. In particular, the cationic paste presents the largest impacts. For instance, in the NLT and the FE impact categories, the cationic paste represents 43.4 % (0.24 m^2) and 59.1 % (0.31 kg P eq.) of the total Impact category, respectively. In order to identify which component of the cationic paste is responsible for this result, a characterization of the cationic paste based on its constituents was carried out. In this analysis, it was observed that the epoxy resin in the formulation of the cationic paste is the main contributor to the majority of the impact categories, being POF = 0.02 kg NMVOC (97.3 % of the total of the impact category), FD = 1.07 kg oil eq. (97.2 %), PMF = 0.009 kg PM10 eq. (96 %), CC = 2.71 kg CO_2 eq. (95.8 %) and TA = 0.016 kg SO_2 eq. (93 %) the most affected categories. This result can be mainly explained due to the direct emissions of air pollutants associated with the resin production process, such as CO_2 from combustion processes (Wilson, 2009).

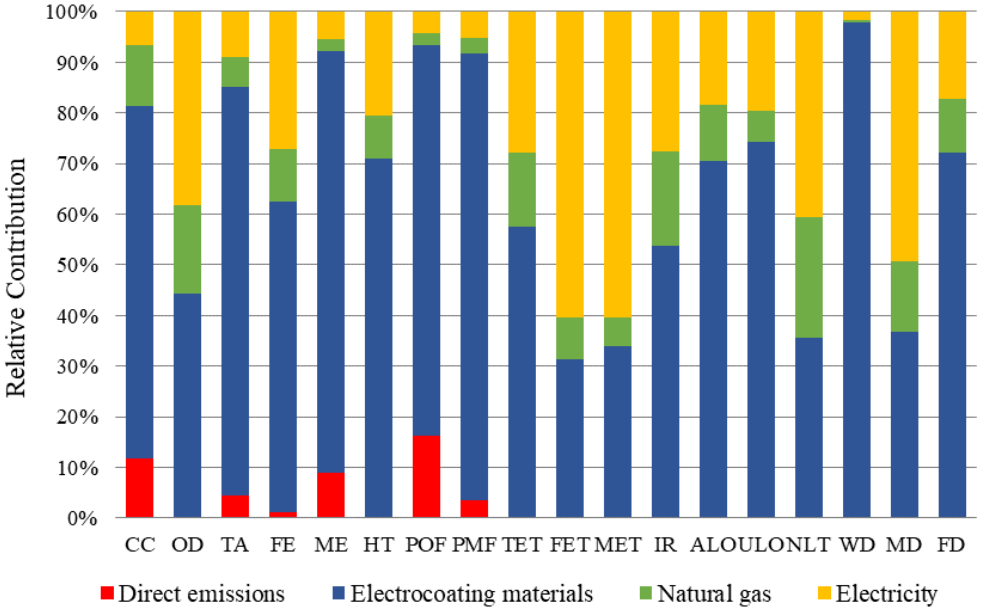


Figure 16. Results of the LCI characterization for the electrocoating process in the Base Case (SS1). Acronyms used in this figure: CC: Climate Change; OD: Ozone Depletion; TA: Terrestrial Acidification; FE: Freshwater Eutrophication; ME: Marine Eutrophication; HT: Human Toxicity; POF: Photochemical Oxidant Formation; PMF: Particulate Matter Formation; TET: Terrestrial Ecotoxicity; FET: Freshwater Ecotoxicity; MET: Marine Ecotoxicity; IR: Ionizing Radiation; ALO: Agricultural Land Occupation; ULO: Urban Land Occupation; NLT: Natural Land Transformation; WD: Water Depletion; MD: Metal Depletion; FD: Fossil Depletion.

3.6.1.2 Characterization primer process Base Case

As can be seen in Figure 17, most of the impact categories are highly affected by natural gas consumption, given its background processes related to its extraction and production, each with a high impact. The direct emissions of the primer process are more relevant than in the electrocoating and have their main contribution to the impact categories of POF = 6.2 kg NMVOC (59.3 %), ME = 0.13 kg N eq. (41.7 %), PMF = 0.73 kg PM10 eq. (25.6 %) and TA = 1.86 kg SO_2 eq. (21.2 %). With regard to the acidification and eutrophication impact categories, the high relevance of the direct emissions can be assigned to the NOx emissions coming from the oxidation process of the recuperative thermal oxidizers installed in the primer ovens, what confirms observations made by Banar and Çokaygi (2010).

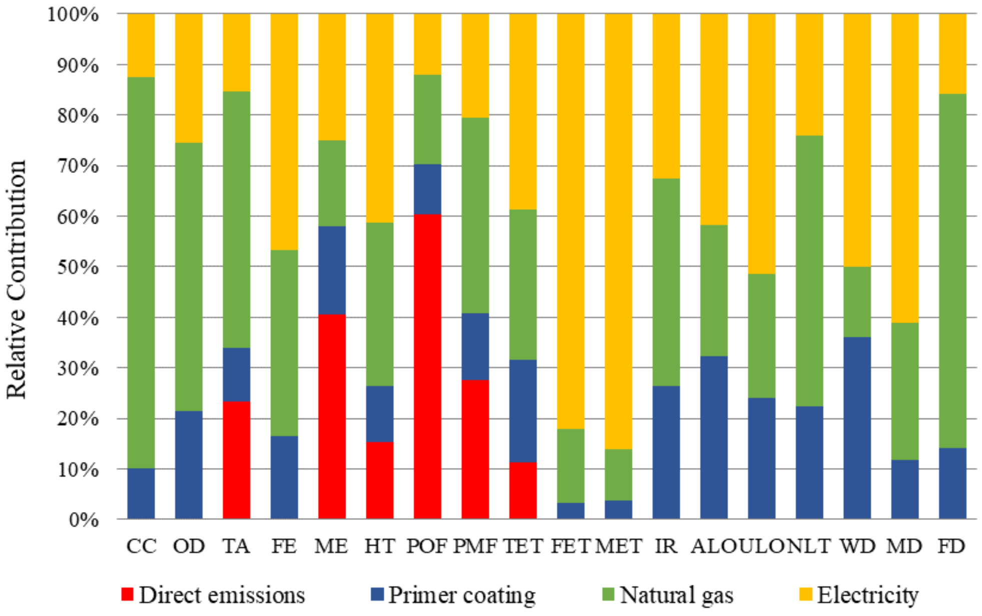


Figure 17. Results of the LCI characterization for the primer process in the Base Case (SS2). Acronyms used in this figure: CC: Climate Change; OD: Ozone Depletion; TA: Terrestrial Acidification; FE: Freshwater Eutrophication; ME: Marine Eutrophication; HT: Human Toxicity; POF: Photochemical Oxidant Formation; PMF: Particulate Matter Formation; TET: Terrestrial Ecotoxicity; FET: Freshwater Ecotoxicity; MET: Marine Ecotoxicity; IR: Ionizing Radiation; ALO: Agricultural Land Occupation; ULO: Urban Land Occupation; NLT: Natural Land Transformation; WD: Water Depletion; MD: Metal Depletion; FD: Fossil Depletion.

3.6.1.3 Characterization topcoat process Base Case

The characterization results of the topcoat process are shown in Figure 18. To simplify the interpretation of the results, all created paint clusters were finally grouped into an individual system namely “Total paints”.

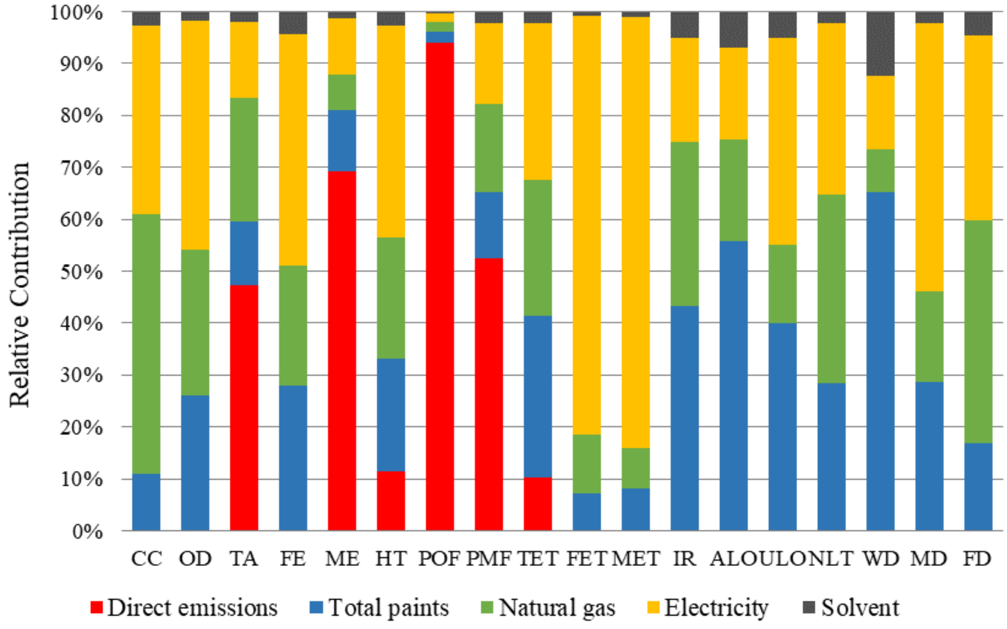


Figure 18. Results of the LCI characterization for the topcoat process in the Base Case (SS3). Acronyms used in this figure: CC: Climate Change; OD: Ozone Depletion; TA: Terrestrial Acidification; FE: Freshwater Eutrophication; ME: Marine Eutrophication; HT: Human Toxicity; POF: Photochemical Oxidant Formation; PMF: Particulate Matter Formation; TET: Terrestrial Ecotoxicity; FET: Freshwater Ecotoxicity; MET: Marine Ecotoxicity; IR: Ionizing Radiation; ALO: Agricultural Land Occupation; ULO: Urban Land Occupation; NLT: Natural Land Transformation; WD: Water Depletion; MD: Metal Depletion; FD: Fossil Depletion.

These results present a similar behavior as for the primer process. Direct emissions considerably increase their relevance in the following impact categories: POF = 237.0 kg NMVOC (94.0 %), ME = 1.37 kg N eq. (69.2 %) and PMF = 7.7 kg PM10 eq. (52.6 %). Moreover, the share of the direct emissions in the TA impact category raises with 19.6 kg SO_2 eq. to 47.2 %, 26 % higher than in the primer process. This trait can be attributed to two reasons. Firstly, the increment of the NOx emissions in the exhaust air of the recuperative thermal oxidizers installed in the basecoat spray booths. In particular, the high contribution of the direct emissions to the TA and ME categories is manifestly connected to the NOx emissions from the oxidation process (Banar and Çokaygi, 2010). Secondly, the increase of the VOC emissions from the topcoat ovens, where the solvent-borne paints are being cured without abatement equipment, unlike the primer process. The high impact of the direct emissions to the POF impact category is reasonable since VOCs are well-known precursors of photochemical smog and tropospheric ozone, as also discussed by Finlayson-Pitts (2000), Xu et al. (2015) and Xu et al. (2016).

As shown in Figure 18, the relevance of the paints in most impact categories notably increased in comparison to the primer process. The highest contributions of the topcoat paints can be observed in WD = 27.8 m^3 (65.3 %), ALO = 64.2 m^2a (55.8 %) and IR = 105.0 kBq U235 eq. (43.4 %), whose relevance can presumably be traced back to the manufacturing process of the paints and to their constituents.

As can be observed in the characterization results for all the sub-processes, natural gas consumption has a relevant influence on almost all impact categories and therefore on the total environmental impact of the painting process. For instance, in the topcoat process, CC = 3897.4 kg CO_2 eq. (49.8 %), FD = 1338.2 kg oil eq. (42.9 %) and NLT = 0.55 m^2 (36.2 %) are the most affected impact categories. Moreover, natural gas plays an important role in the OD impact category with a relevant contribution of 28.1 %. The contributions of the natural gas to the CC, FD and OD impact categories were already reported in other studies (Skone et al., 2016; Tomatis et al., 2019).

3.6.2 Characterization Scenario A

Scenario A includes the reduction of free formaldehyde in the paints´ composition introduced by the paint manufacturers and the technical and operational modifications in the primer process. Comparing the characterization results of the overall painting process in Scenario A to those of the Base Case, it can be seen that the change in the paints did not significantly decrease the impacts of the topcoat process. This can be observed in all impact categories, which reduced their values by less than 0.1 %.

The major improvements introduced in Scenario A were the reduction of the formaldehyde emissions in primer process by discharging the primer flash off waste gas into the primer oven and increasing the temperature of the primer oven abatement systems. Increasing the temperature of the abatement installations involves a relevant increase of the natural gas consumption. This higher consumption leads to a dramatical increase in almost all impact categories. The most affected categories are ME, with an increase of 62.2 % from 0.31 kg N eq (Base Case) to 0.51 kg N eq (Scenario A), PMF (Base Case = 2.85 kg PM10 eq; Scenario A = 4.14 kg PM10 eq; 45.7 %), TA (Base Case = 8.78 kg SO_2 eq; Scenario A = 12.45 kg SO_2 eq; 41.8 %) and CC (Base Case = 2735 kg CO_2 eq; Scenario A = 3129 kg CO_2 eq; 14.4 %). With regard to the ME and TA impact categories, the raise can be attributed to the higher NOx emissions as a result of the temperature increase (Banar and Çokaygi, 2010).

The main objective in reducing the formaldehyde emissions is to achieve an improvement in the human toxicity (HT) impact category. Therefore, the comparison of the HT in the two scenarios was made and the results are illustrated in Figure 19.

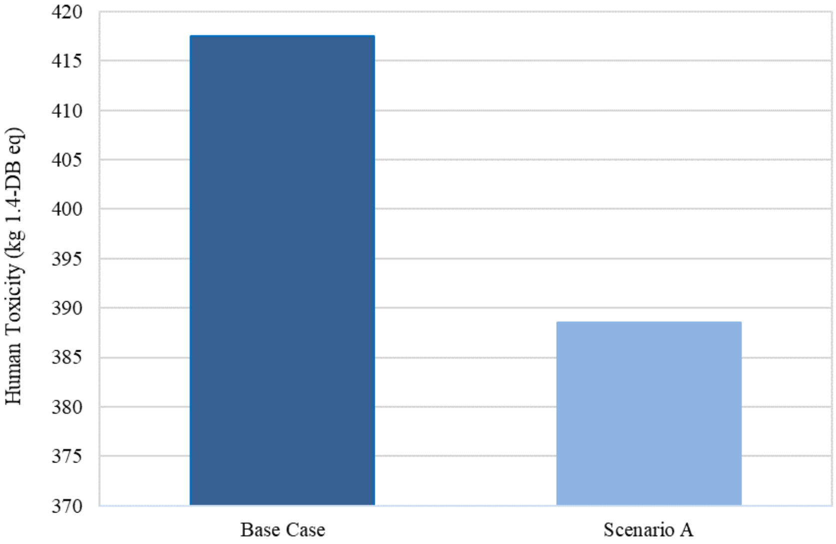


Figure 19. Results of the LCI characterization for the overall painting process in Base Case and Scenario A. Comparison HT values for the primer subsystem.

The figure shows the characterization results of the overall painting process for the HT impact category with the focus on the primer subsystem. HT considerably decreases its impact from

417.5 kg 1,4-DB eq in the Base Case to 388.5 kg 1,4-DB eq in the in the Scenario A, which corresponds to a reduction of 7 %. Besides, the terrestrial ecotoxicity (TET) impact category is also decreased by 4 %. The reduction of the toxicity related impact categories confirms that the target of the implemented actions in Scenario A is met.

3.6.3 Characterization Scenarios B and C

A characterization of the two proposed scenarios, Scenario B and C, considering the topcoat process was performed and the results compared to Scenario A. For the majority of the impact categories, an increase can be observed when the RTO scenario (Scenario B) is compared to Scenario A. On the contrary, most of the categories decrease their values when the scenario with the recuperative oxidizers (Scenario C) is compared to Scenario A. The highest differences could be found for CC (Scenario A = 7715 kg CO_2 eq; Scenario B = 8407 kg CO_2 eq; Scenario C = 7082 kg CO_2 eq), FD (Scenario A = 3056 kg oil eq.; Scenario B = 3294 kg oil eq.; Scenario C = 2839 kg oil eq.), NLT (Scenario A = 1.48 m^2; Scenario B = 1.58 m^2; Scenario C = 1.39 m^2), IR (Scenario A = 230.0 kBq U235 eq.; Scenario B = 243.6 kBq U235 eq.; Scenario C = 217.6 kBq U235 eq.), OD (Scenario A = 1.036×10^{-3} kg CFC 11 eq.; Scenario B = 1.089×10^{-3} kg CFC-11 eq.; Scenario C = 0.987×10^{-3} kg CFC-11 eq.), and TET (Scenario A = 0.647 kg 1,4-DB eq.; Scenario B = 0.633 kg 1,4-DB eq.; Scenario C = 0.572 kg 1,4-DB eq.).

Regarding the reduction of the HT, the main objective of the installation of the abatement system, the results obtained for Scenario A and the two abatement scenarios are: Scenario A = 1329 kg 1,4-DB eq.; Scenario B = 1284 kg 1,4-DB eq.; Scenario C = 1176 kg 1,4-DB eq. A reduction in the HT category was achieved by both scenarios, with a decrease being significantly higher for the recuperative thermal oxidizers compared to the RTO (11.5 % and 3.4 % reduction, respectively). Furthermore, in the impact categories ME (Scenario A = 1.94 kg N eq.; Scenario B = 2.81 kg N eq.; Scenario C = 2.77 kg N eq.), PMF (Scenario A = 14.46 kg PM10 eq.; Scenario B = 19.69 kg PM10 eq.; Scenario C = 18.83 kg PM10 eq.) and TA (Scenario A = 41.0 kg SO_2 eq.; Scenario B = 54.9 kg SO_2 eq.; Scenario C = 51.6 kg SO_2 eq.), an increment was observed for both proposed systems but a higher increase is caused by the RTO. In order to better illustrate these results, Table 23 shows the variation of the characterization values in percentage for all impact categories.

Table 23. Variation in percentage of the characterization results for all impact categories in the Scenarios B and C with regard to Scenario A for the topcoat process. Acronyms used in this figure: CC: Climate Change; OD: Ozone Depletion; TA: Terrestrial Acidification; FE: Freshwater Eutrophication; ME: Marine Eutrophication; HT: Human Toxicity; POF: Photochemical Oxidant Formation; PMF: Particulate Matter Formation; TET: Terrestrial Ecotoxicity; FET: Freshwater Ecotoxicity; MET: Marine Ecotoxicity; IR: Ionizing Radiation; ALO: Agricultural Land Occupation; ULO: Urban Land Occupation; NLT: Natural Land Transformation; WD: Water Depletion; MD: Metal Depletion; FD: Fossil Depletion.

Impact category	Scenario B %	Scenario C %
CC	**9.0**	**-8.2**
OD	**5.1**	**-4.7**
TA	**34.0**	**25.8**
FE	**4.2**	**-3.9**
ME	**44.8**	**42.5**
HT	**-3.4**	**-11.5**
POF	**-2.7**	**-3.2**
PMF	**36.1**	**30.2**
TET	**-2.1**	**-11.5**
FET	**2.0**	**-1.9**
MET	**1.4**	**-1.3**
IR	**5.9**	**-5.4**
ALO	**3.7**	**-3.4**
ULO	**2.8**	**-2.5**
NLT	**6.7**	**-6.1**
WD	**1.5**	**-1.4**
MD	**3.2**	**-3.0**
FD	**7.8**	**-7.1**

Impact categories that increase their impact in comparison with the Scenario A are written in red. The green values represent the categories that were reduced in Scenario B and/or C, respectively, with regard to Scenario A.

All in all, the characterization results indicate that, from the two proposed topcoat oven abatement scenarios, the installation of an RTO is the less beneficial from the environmental impact perspective. This result can be explained by the fact that the installation of eight recuperative oxidizers implies an overall reduction in natural gas consumption due to the energy recovery in the heating of the drying ovens with the excess heat from the combustion process. The installation of the RTO implies an overall increase in the natural gas consumption of the Plant, which leads to an increase of the total environmental impact. This observation is in line with the results obtained by Tomatis et al. (2019), who compared two abatement systems, i.e., an RTO and a catalytic thermal oxidizer, to an outdated thermal oxidizer. In this study, the auxiliary fuel used to run the equipment was also identified as the major contributor to the overall environmental impact. This study also highlighted the significant role of natural gas to the HT impact category and explains the higher decrease in HT obtained by the recuperative thermal oxidizers due to the lower natural gas needs.

The characterization values indicated above for the HT impact category were also represented for the three scenarios to better visualize the results (Figure 20).

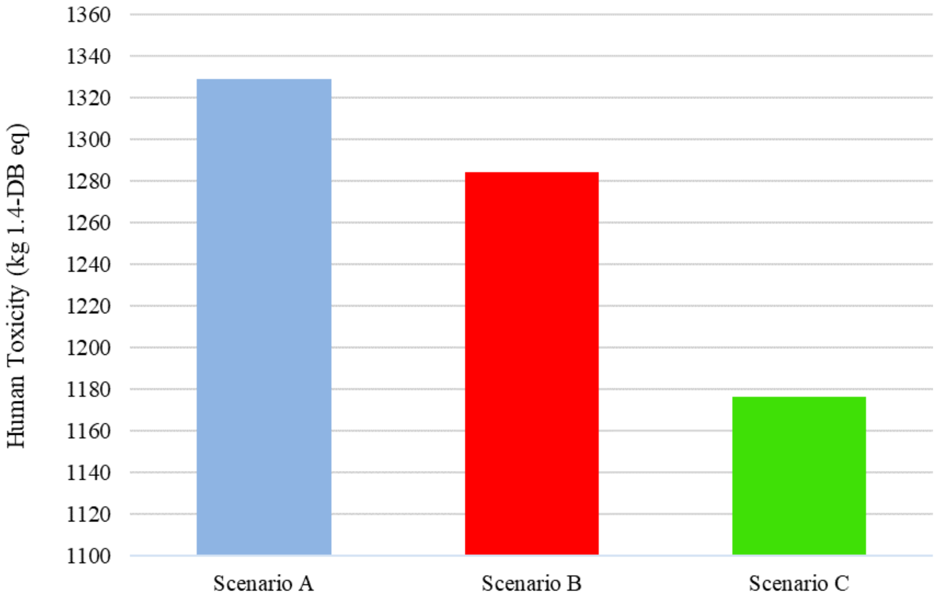


Figure 20. Results of the LCI characterization for the HT impact category in the topcoat process, Scenarios A, B and C.

3.6.4 Characterization Scenario D

The characterization step of the topcoat process was finally conducted for Scenario D. Scenario D was applied based on Scenario B with the addition of one recuperative thermal oxidizer for the abatement of the basecoat spray booth waste gas. This modification achieved a reduction of VOC and formaldehyde emissions but implied a significant increase in the natural gas consumption and the subsequent raise in the CO and NOx emissions. This led to an increase in the characterization values in almost all impact categories. The most affected categories were ME, with an increase of 46.4 % in comparison to Scenario B, TA (34.7 %) and PMF (37.7 %). On the other hand, the reduction of VOC emissions caused a decrease in the POF impact category of 19.7 %. These results are in line with the observations made in the previous scenarios.

The characterization results of the topcoat process for the HT impact category of Scenarios B, C and D were also represented to show the variation of this category achieved by the implementation of Scenario D.

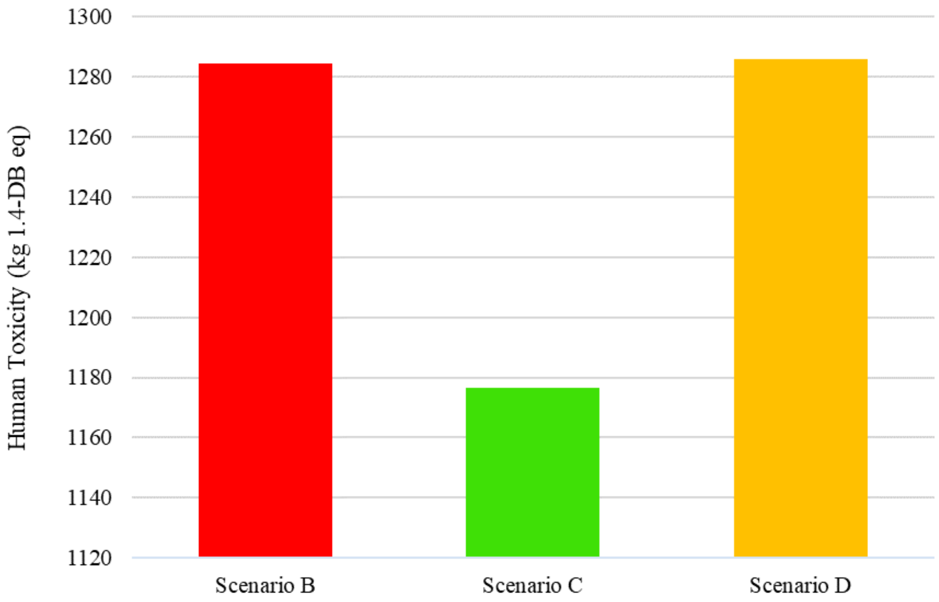


Figure 21. Results of the LCI characterization for the HT impact category in the topcoat process, Scenarios B, C and D.

As can be seen in Figure 21, the implementation of Scenario D does not achieve the pursued reduction of the HT impact category, with a result very close to that of Scenario B (0.1 % higher) and significantly higher than Scenario C (9.3 % higher). This can be clearly attributed to the increase of the natural gas consumption of Scenario D. While the reduction of formaldehyde would reduce the HT impact category, this decrease is compensated by the increase caused by the additional natural gas needed to operate the abatement system considered in Scenario D.

3.6.5 Normalization all scenarios – comparative results

To allow a better comparison of the total environmental impact and the HT impact category of the different scenarios, the characterization results were normalized, and the results of this step are shown in this section.

Initially, the results of the 18 impact categories were analyzed. In a following step, the two criteria described in the methodology section were applied. Firstly, the most relevant impact categories were selected, i.e., the categories with a relevant contribution to the total environmental impact above 2 %, and secondly, the HT impact category only, since the reduction of human toxicity through the reduction of formaldehyde emissions is the main objective of the different scenarios.

Figure 22 represents the normalized index of the overall painting process considering the relevant impact categories for the different scenarios.

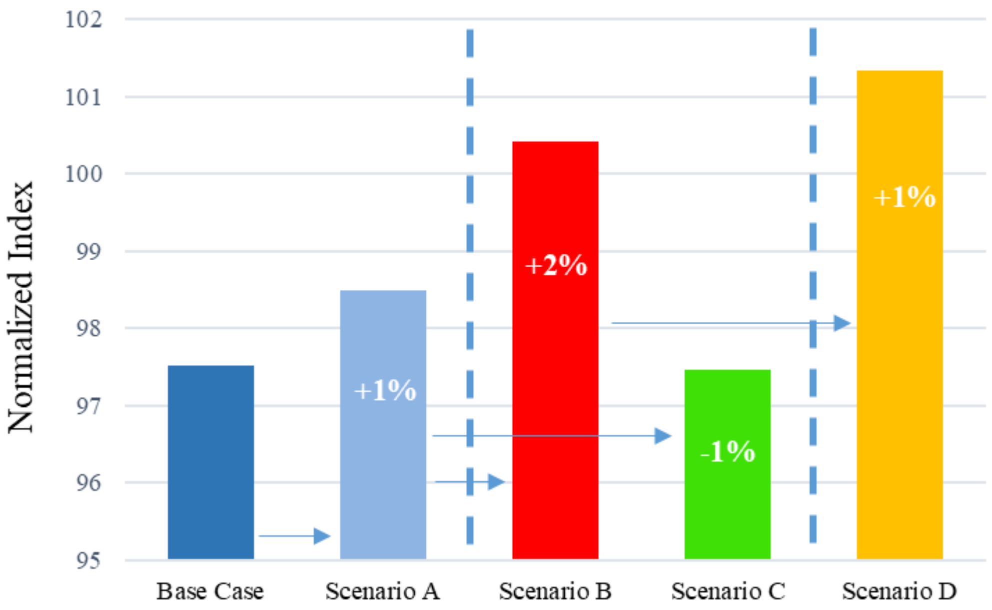


Figure 22. Results of the normalization of the overall painting process for all studied scenarios – selected relevant impact categories.

The selected impact categories were TA, FE, HT, POF, FET, MET, NLT and FD. All together represent 95.5 % of the total normalized index.

An increase of the normalized index from 97.5 in the Base Case to 98.5 in Scenario A is observed, which corresponds to a raise of 1 %. This demonstrates that even though a reduction of the formaldehyde emissions, mainly in the primer process, was achieved by Scenario A, the implementation of this scenario causes an increase of the environmental impact of the paint shop. A more critical situation is found for Scenario B, which increases its normalized index by 2 % (100.4) starting from Scenario A as a basis. As discussed for the characterization results, the overall increase of the natural gas consumption in Scenario B is responsible for this deterioration. On the contrary, the implementation of Scenario C causes a reduction of 1 % (97.5 %) from the Scenario A. The reduction of the natural gas needs of the paint shop in this scenario leads to an improvement of the environmental impact which brings the normalized index to the initial situation before the implementation of any actions (Base Case). Finally, the application of Scenario D implies an increase of 1 % of the normalized index (101.4) from Scenario B as a basis. The increase of natural gas needed to start up the additional recuperative oxidizer in Scenario D is responsible for this increment. Similar effects were observed when considering the 18 impact categories.

In this context, the ultimate objective of different actions is the reduction of formaldehyde emissions and therefore the reduction of the human toxicity impact category. Consequently, the normalization data for the HT impact category was represented for all scenarios.

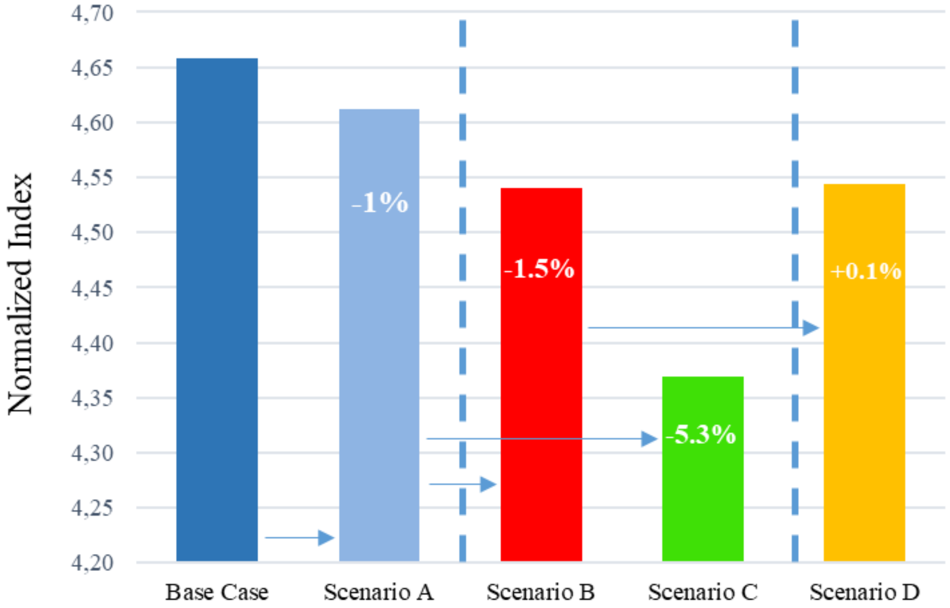


Figure 23. Results of the normalization of the overall painting process for all studied scenarios - Human Toxicity (HT) impact category.

The results represented in Figure 23 confirm that all studied scenarios achieve a reduction in the HT impact category if they are compared with the Base Case. However, the magnitude of this reduction is different for the different scenarios. Scenario A slightly reduces the normalized index for the HT category by 1 % (Base Case = 4.65; Scenario A = 4.61). The reduction of formaldehyde emissions causes a decrease of HT but the increase in natural gas consumption almost compensates this decrease.

When it comes to the implementation of Scenario B (RTO) or Scenario C (recuperative thermal oxidizers) for the topcoat ovens, the benefits in terms of HT of Scenario C over B are clearly demonstrated. Scenario B achieves a reduction of 1.5 % in the normalized index with regard to Scenario A (Scenario A = 4.61; Scenario B = 4.54), while in the case of Scenario C a decrease of 5.3 % was achieved (Scenario A = 4.61; Scenario C = 4.37). The difference in the reduction on human toxicity can be explained once again by the difference in natural gas consumption of both alternatives. The reduction in formaldehyde emissions was achieved by both technologies; however, the increase in natural gas consumption due to the installation of the RTO implies a smaller decrease in the HT Impact category than for the recuperative oxidizers, as observed by the characterization results.

Finally, the implementation of Scenario D does not involve a significant variation of HT in comparison with its starting point, the Scenario B. The improvement in the HT caused by the reduction of VOC and formaldehyde emissions is compensated by a deterioration due to the increase of the natural gas consumption.

3.7 CONCLUSIONS

Life Cycle Assessment (LCA) was applied to analyze the environmental impacts of the vehicle painting process and to compare these impacts before and after the introduction of different actions to reduce formaldehyde emissions in the affected areas identified in chapter 2. As regards the two topcoat oven abatement technologies evaluated, the LCA allows the identification of the most environmentally sustainable alternative providing relevant information for the selection during the planning process.

Based on the results obtained in the LCA and the interpretations and discussion given in this chapter, the following conclusions can be drawn:

- Analyzing the hot spots from the overall painting process it can be concluded that the topcoat process causes the highest environmental impacts. This result is attributed to the significant consumption of materials and production of emissions of this sub-process, the higher consumption of natural gas, and the direct emissions into the atmosphere without installed abatement systems. Improvements in the production of paints and their constituents itself, for instance by reducing the solvent content or replacing substances by less harmful alternatives, should be further strived by paint manufacturers to reduce the environmental impacts of vehicle paints shops.
- Furthermore, the electrocoating was also identified as a process that causes a relevant environmental impact in the paint shop. In particular, the epoxy resin used in the cationic paste is the main responsible for the environmental impacts of this process. Therefore, a possible future action for paint manufacturers should be the research and development of alternative resins that can be used to produce electrocoating materials with a lower environmental impact, or a modification in their production process leading to a reduction of the CO_2 emissions.
- Scenario A introduces a reduction of the formaldehyde emissions, mainly in the primer process, by treating the flash off emissions and increasing the temperature of the oven abatement systems. Comparing the results of Scenario A to the original situation of the paint shop (Base Case), a decrease of 7 % of the HT impact category can be observed in the primer process. Consequently, Scenario A achieves the pursued reduction of the human toxicity. However, the higher natural gas consumption led to an increase in almost all other impact categories.
- Scenarios B and C studied two different abatement technologies, i.e., regenerative thermal oxidation and recuperative thermal oxidation, currently used in vehicle paint shops across the world for the elimination of VOCs and, particularly, formaldehyde emissions. Comparing both scenarios with Scenario A, it can be concluded that:
  - While both abatement technologies achieved a decrease in the human toxicity due to the reduction of formaldehyde emissions, the implementation of recuperative thermal oxidizers (Scenario C) reached a more significant human toxicity reduction than the regenerative thermal oxidation technology (Scenario B) (5.3 % and 1.5 % reduction of the normalized index in the HT impact category for the overall painting process, respectively).
  - The recuperative thermal oxidizers (Scenario C) achieved an overall improvement when considering the most relevant impact categories selected in this study, unlike the regenerative thermal oxidizer (Scenario B) (1 % reduction of the normalized index observed for the recuperative thermal oxidizers against 2 % increase for the regenerative thermal oxidizer when considering the complete painting process).
    - These results can be mainly explained by the higher overall energy consumption of the regenerative thermal oxidation technology. Thus, the installation of the

recuperative thermal oxidizers is the most environmentally sustainable alternative.

- Scenario D reduces the VOC and formaldehyde emissions. However, it does not achieve a reduction of the HT impact category, with a result very close to that of Scenario B and significantly higher than Scenario C. This can be attributed to the increase of the natural gas consumption of Scenario D.
- All improvement scenarios aimed at reducing the emissions of formaldehyde and thus the HT impact category. The results obtained in the LCA confirm that all studied scenarios achieve the pursued reduction if they are compared to the Base Case. However, the magnitude of this reduction is different for the different scenarios. The subsequent implementation of Scenario A followed by Scenario C represents the most environmentally sustainable option in view of both human toxicity and the total environmental impact. The target of the Industrial Emissions Directive to protect the environment is achieved through the implementation of the actions proposed in these two scenarios.

All in all, these results provide valuable information to the company for the selection of the most suitable actions to reduce formaldehyde emissions. LCA has been confirmed as a powerful tool that can be applied during the planning and selection activities to evaluate and identify the most environmentally sustainable technology. Nevertheless, the economic aspect has not yet been included in the evaluation. The eco-efficiency analysis conducted in chapter 4 considers the costs for implementation of the Scenarios B or C an provides the company with additional input for the decision-making.

4 ECO-EFFICIENCY ANALYSIS OF ABATEMENT EQUIPMENT FOR FORMALDEHYDE EMISSIONS REDUCTION

The study conducted in chapter 2 explained the necessity to implement specific actions in paint shop 3 to reduce the formaldehyde emissions below the applicable emission limit value. The Life Cycle Assessment described in chapter 3 demonstrated that the sequential implementation of the actions included in Scenario A (reduction of free formaldehyde in paints, removal of primer flash off emissions and increasing the primer oven abatement temperature) and Scenario C (installation of recuperative thermal oxidizers for the topcoat ovens) not only ensures meeting the legal requirements, but also reduces the overall environmental burdens of the paint shop. On the contrary, the combination of Scenario A and Scenario B (installation of an RTO for the topcoat ovens) implies an increase of the total environmental impact of the paint shop while ensuring legal compliance regarding formaldehyde emissions.

For the selection of the most suitable abatement technology, i.e., RTO or recuperative thermal oxidation, not only the environmental sustainability aspect can be considered by the company. Beside the technical and environmental evaluation also an economic assessment of the potential solutions is of importance for decision making. Eco-efficiency assessment is a quantitative tool to study the environmental impacts of a system in conjunction with its economic value (ISO 14045:2012) and helps entities to make conscious decisions (Torregrossa et al., 2018; Ramírez-Melgarejo et al., 2021). Thus, eco-efficiency analysis establishes a connection between the ecological impact of a system and its economic dimension (Desli et al., 2021).

In this chapter, an eco-efficiency analysis of the two abatement options for the topcoat ovens was performed to introduce the cost factor into the evaluation and support the company in the decision-making process. Furthermore, considering the results obtained in this and the

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previous chapters, a proposal for the best eco-efficient paint shop in view of formaldehyde emissions performance is given.

4.1 OBJECTIVES

The main objectives of this chapter are:

- Perform an economic evaluation of the two abatement options for the topcoat ovens as described in Scenario B and Scenario C of chapter 3.
- Carry out an eco-efficiency analysis using the results of the LCA of chapter 3 and the economic evaluation.
- Define the most environmentally sustainable and the most economically favorable abatement option.
- Explain the final decision of the company.
- Make a proposal for the best eco-efficient paint shop in view of formaldehyde emissions performance.

4.2 SCOPE

The eco-efficiency analysis was performed to compare the two abatement options included in Scenario B and Scenario C described in chapter 3. Both scenarios were evaluated as alternatives to reduce the high formaldehyde emissions from the waste gas of the topcoat ovens of paint shop 3, as confirmed by the investigation conducted in chapter 2. Scenario B corresponds to the installation of a 5-bed RTO, while Scenario C implies the installation of eight recuperative thermal oxidizers. Figure 24 represents the different scenarios to simplify the interpretation of the results.

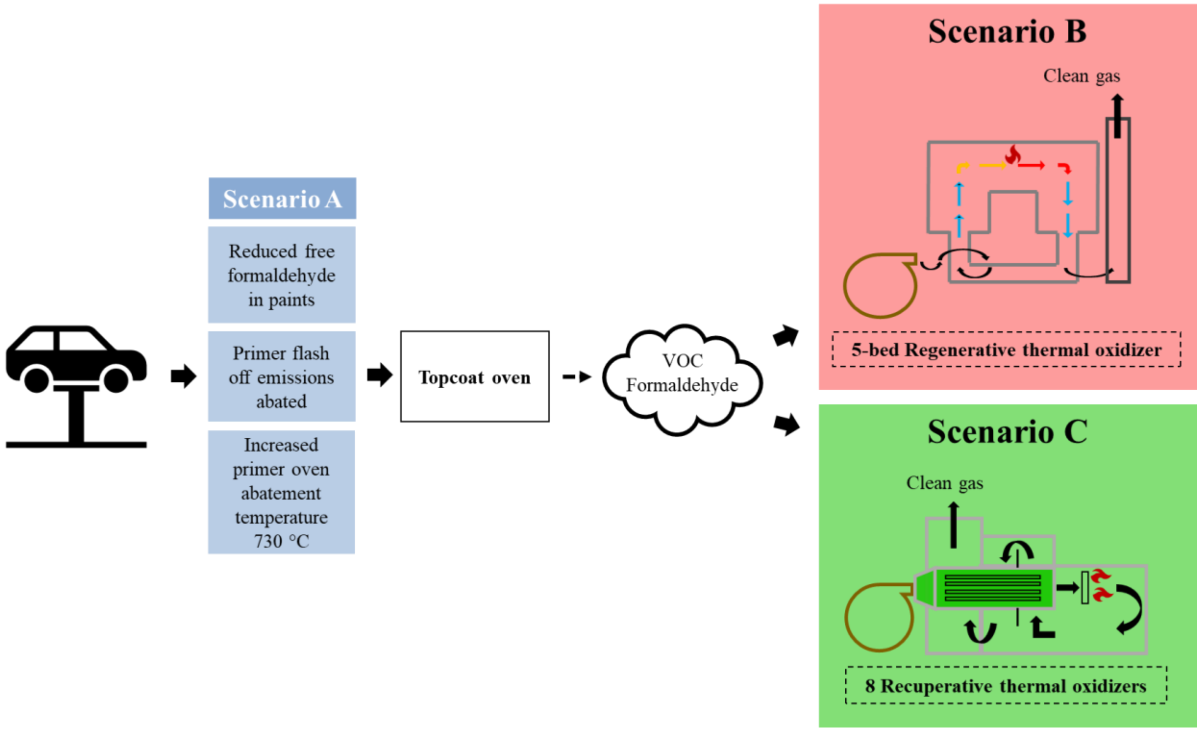

Figure 24. Illustration of Scenarios B and C with Scenario A as starting point as studied in the eco-efficiency analysis.

4.3 METHODOLOGY

As a prerequisite for the eco-efficiency analysis, an initial study of the two abatement systems was performed, including an economic evaluation to obtain all necessary economic data. The capital costs for the installation of the two systems were requested from equipment manufacturers for the paint shop studied. The operational and maintenance costs data were available from other company plants with similar equipment. These costs were calculated for the whole lifespan of the installations and the annual increase in the cost of natural gas (OMIP, 2018) and spare parts for equipment was taken into account using the average inflation rates of recent years of the country where the paint shop is located (INE, 2017). A detailed calculation of the natural gas costs is given in Appendix 5. Finally, the total costs were normalized to the functional unit to allow the comparison between the two systems.

The eco-efficiency analysis was conducted based on the criteria prescribed in the ISO 14045:2012. The analysis was performed with the focus set on the topcoat process, for which the abatement equipment was planned. The normalization results previously obtained in the LCA were used for the eco-efficiency evaluation. Two different indicators were selected and represented against the total cost per hour:

- Variation of the normalized index, expressed in percentage, considering the sum of the impact categories with a relevant contribution to the total environmental impact greater than 2 % in the normalization results.
- Variation of the normalized index, expressed in percentage, of the HT impact category.

It must be highlighted that, even though the LCA did not consider the construction of the painting installations but only the operation of the equipment, the costs for the installation of the two planned abatement systems could not be excluded. They are the major cost factor in the total calculated costs of the two systems and are necessary to achieve a representative comparison. Besides, all other painting equipment and installations were already available in the paint shop at the time of this study and no additional investment would be necessary.

4.4 RESULTS AND DISCUSSION

The results of the economic evaluation are summarized in Table 24.

Table 24. Implementation costs for RTO and Recuperative Thermal Oxidizers.

	Scenario B: RTO	Scenario C: Recup. Oxidizers	Unit
Lifetime	25	15	Years
Installation cost	7.3	25	Million €
Maintenance	84000	43200	€ / Year
Natural gas	56.3	-52.3	€ / h
Total cost / h	**136.85**	**305.36**	€ / h

The difference observed in the lifetime of the two abatement systems is inherent to the type of equipment. Recuperative oxidizers have more parts that deteriorate over time, and after several years an exchange or repair is no longer possible. Consequently, the complete equipment needs to be replaced. Regarding the installation cost, the much higher value shown for the recuperative oxidizers is due to the fact that, for this technology, eight pieces of equipment would be needed to treat the complete waste gas from the topcoat ovens. This implies the installation of the eight systems together with their corresponding heat exchangers and burners. Additionally, the existing burners to heat the ovens would be shut down and removed, which increases the cost. In the case of the RTO, only one larger system with 5 ceramic beds and three burners would be sufficient. It was calculated that one hour of operation of the RTO implies a cost of 136.85 € while for the eight recuperative thermal oxidizers, the costs reach 305.36 €.

The results of the eco-efficiency analysis are represented in Figure 25 for the selected relevant impact categories and Figure 26 for the HT impact category. The percentage variation of the normalized index has been assessed with the calculated total costs in € per hour of operation for both types of technology. Considering all selected relevant impact categories (Figure 25), it can be recognized that the installation of the recuperative thermal oxidizers to reduce formaldehyde emissions is the most environmentally sustainable alternative (it leads to a 2.6 % reduction of the normalized index against a 3.1 % increase for the RTO), although the costs are 2.2 times those of the RTO. On the other hand, the most economically favorable abatement technology is the installation of the RTO.

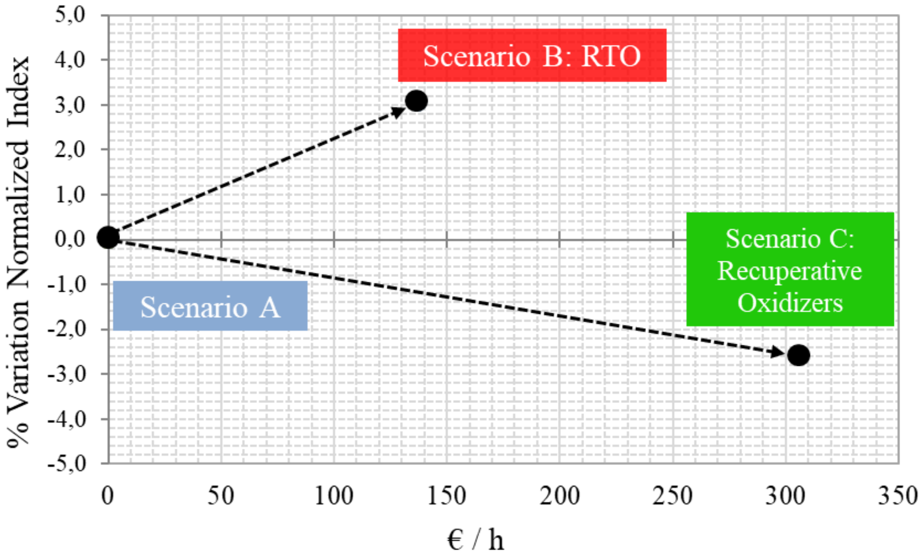

Figure 25. Results of the eco-efficiency analysis for the topcoat process: selected relevant impact categories.

Regarding the reduction of the HT impact category, the two technologies can also be compared from the perspective of eco-efficiency in Figure 26.

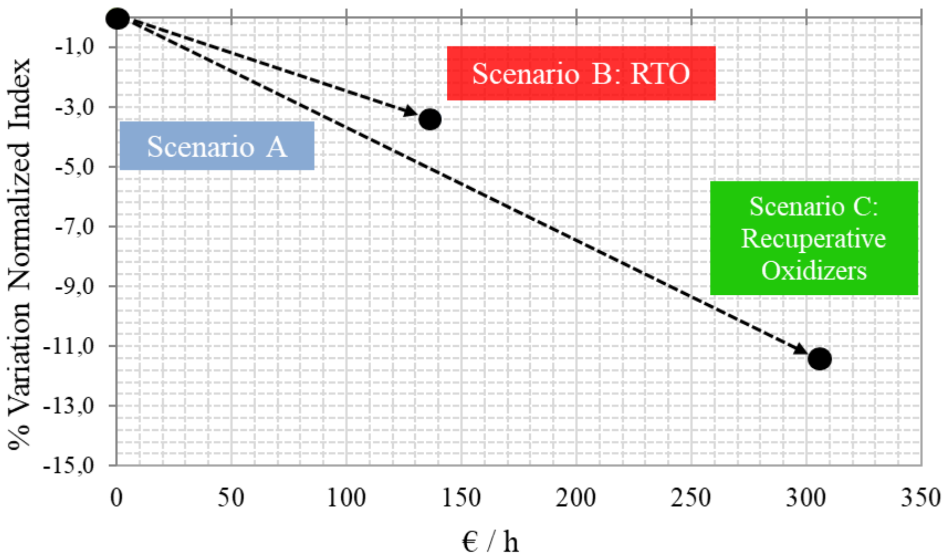

Figure 26. Results of the eco-efficiency analysis for the topcoat process: Human Toxicity (HT).

This graph clearly illustrates the difference in the reduction of the human toxicity achieved by both technologies considering their implementation costs. Even though a reduction is obtained by both technologies, the costs to gain a reduction of more than 10 % of the HT impact category for the topcoat process are much higher for the implementation of the eight recuperative thermal oxidizers (305.36 €/h and 136.85 €/h, respectively). From these results, it can be concluded that the implementation of the recuperative thermal oxidizers is a better solution if a higher reduction of the human toxicity is pursued and the higher costs are not a relevant factor.

4.5 FINAL DECISION OF THE COMPANY

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4.6 PROPOSAL FOR BEST ECO-EFFICIENT PAINT SHOP IN VIEW OF FORMALDEHYDE EMISSIONS PERFORMANCE

The investigation conducted in this Ph.D. thesis allowed to identify the areas and processes of the vehicle paint shop from which high formaldehyde emissions into the atmosphere occur. Once these processes were identified, actions to reduce the emissions could be proposed and evaluated from a technical, environmental and economic perspective. This supported the company in the planning process to select the best options to reduce the formaldehyde emissions and comply with the applicable legislation while achieving a right balance between environmental protection and cost efficiency. The outcomes of this research can also be applied to propose a general layout or setting for the best eco-efficient paint shop in view of formaldehyde emissions performance. The main characteristics of this paint shop are summarized in Table 25.

Table 25. Proposal for best eco-efficient paint shop in view of formaldehyde emissions performance

Process / Area	Formaldehyde emissions	Best setting
Electrocoating baths	Not relevant	Not relevant
Electrocoating ovens	> ELV[1] 2 mg/m3	Abatement system necessary[*]: RTO @ > 810 °C or Recup. Oxidizers @ > 700 °C
Primer spray booth	Not relevant for WB[2] primer	Not relevant
Primer flash off zone	≥ ELV[1] 2 mg/m3	Flash off emissions to be treated at primer oven abatement system
Primer ovens	> ELV[1] 2 mg/m3	Abatement system necessary[*]: RTO @ > 810 °C or Recup. Oxidizers @ > 700 °C
Basecoat spray booth	Not relevant either for WB[2] or SB[3] paints	No abatement system installed if not legally required. Abatement significantly increases overall environmental impact.
Basecoat intermediate flash off zone	≥ ELV[1] 2 mg/m3	Flash off emissions to be treated at topcoat oven abatement system.
Clearcoat spray booth	Not relevant for SB[3] clearcoat	No abatement system installed if not legally required. Abatement significantly increases overall environmental impact.
Topcoat ovens	>> ELV[1] 2 mg/m3	Abatement system necessary[*]: **Recup. Oxidizers @ > 700 °C with excess heat recovery to heat the ovens**
Other processes (PVC sealing, waxing)	≥ ELV[1] 2 mg/m3 (if exhaust systems interconnected with other areas or contaminated with paint and sludge rests)	Avoid leaks from other areas and regular cleaning of exhaust systems

[1] Emission Limit Value

[2] Water Based

[3] Solvent Based

[*] Frequent maintenance and repairs necessary to avoid efficiency loss.

The distinctive characteristic of the work carried out in this Ph.D. thesis is the fact that all data were collected under the operating conditions of real vehicle paint shops. This has by nature several limitations that are intrinsic to this kind of studies. For instance, the LCA and the subsequent eco-efficiency analysis described in chapter 3 and chapter 4 were carried out for a paint shop applying solvent based paints. This was necessary due to the high levels of formaldehyde found in different areas of this paint shop, as discussed in chapter 2. However, a similar study might be conducted for a water-based paint shop in future research to evaluate the differences and confirm the results of this work in another paint shop.

Furthermore, a growing number of paint shops are starting to install new paint shop concepts that considerably contribute to energy savings. Several plants have eliminated in the last 10 to 15 years the primer oven by applying the three-wet concept (Silva Cavalcante et al., 2020). In this process, the application of primer, basecoat and clearcoat is performed without intermediate drying oven, with the consequent energy saving (STS BREF, 2020). In the LCA and eco-efficiency analysis conducted in this Ph.D. thesis, the paint shop analyzed applied the conventional painting steps with an intermediate curing step of the primer coating before the application of the basecoat paint. A future investigation could also be undertaken in a paint shop that applies the three-wet concept.

Finally, one additional improvement that was not analyzed in this work but could be examined in a future study is the introduction of heat recovery at the stacks of the RTO planned for the topcoat ovens. The energy surplus of the eight recuperative thermal oxidizers considered was recovered to heat the drying ovens. However, with regard to the RTO, the energy excess of the hot cleaned gases from this abatement system was not recovered to be used in other paint shop processes. This possibility was disregarded by the paint operator due to space, timing and monetary limitations. Nevertheless, future research could include the addition of heat exchangers to recover the energy excess from the stacks of the RTO, decreasing the energy consumption of the paint shop and thus reducing the overall environmental impact.

4.7 CONCLUSIONS

In this chapter, the economic evaluation and eco-efficiency analysis performed to compare the two abatement options for the topcoat ovens of paint shop 3 were described. The economic evaluation allowed to obtain all cost data necessary to carry out the eco-efficiency analysis, including installation, operational and maintenance costs of the two abatement systems over their lifetime.

The eco-efficiency analysis shows that in cases where only the reduction of the formaldehyde emissions along with an overall improvement of the human toxicity are pursued and the costs are the main factor in the decision-making process, the RTO is the most economically favorable abatement option. On the contrary, considering the overall environmental impact represented by the selected relevant impact categories, it could be demonstrated that the installation of the recuperative thermal oxidizers to reduce formaldehyde emissions is the most environmentally sustainable alternative (it leads to a 2.6 % reduction of the normalized index against a 3.1 % increase for the RTO considering the topcoat process), although the costs are 2.2 times those of the RTO (305.36 €/h and 136.85 €/h, respectively).

The decision of the company to install an RTO at the topcoat ovens of paint shop 3 can be justified by these results. Even though the installation of the recuperative thermal oxidizers achieves an improvement of the environmental performance of the paint shop, the costs to implement this scenario are much higher than those of the scenario with the RTO. Bearing in mind that the installation timeframe of the RTO is significantly shorter and, unlike the recuperative oxidizers, the RTO can be built in parallel to production, the decision of the company is reasonable.

Ultimately, in this chapter a proposal for the best eco-efficient paint shop in view of formaldehyde emissions performance was given. This proposal includes all the knowledge and outcomes acquired in this Ph.D. thesis and considers the installation of recuperative thermal oxidizers for the topcoat ovens as the best option to reduce the formaldehyde emissions while achieving a reduction of the environmental impact of the paint shop.


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GENERAL CONCLUSIONS

Formaldehyde was reclassified in 2015 in the European Union as a substance with a higher carcinogenic category. With this change, all industries covered under the Industrial Emissions Directive 2010/75/EU shall, as far as possible, replace formaldehyde with less harmful substances. If formaldehyde emissions cannot be avoided, significantly more stringent Emission Limit Values must be respected. This affects the painting operations in the automotive industry due to the presence of melamine resins in the paints´ composition. Thus, vehicle manufacturers were obliged to evaluate their legal situation and implement technical and operational countermeasures to reduce or eliminate formaldehyde emissions. The company Opel needed to assess the impact of the mentioned reclassification on its environmental legal compliance and its economic repercussions.

This industrial Ph.D. thesis had the main objectives to gain a deep understanding of the formaldehyde emissions in paint shops of vehicle manufacturing plants from both an environmental and a legal compliance perspective, to propose and evaluate different possibilities for the reduction or elimination of these emissions, including a Life Cycle Assessment, an economic evaluation and a subsequent eco-efficiency analysis to determine the most environmentally sustainable option, and ultimately, to formulate a proposal for the best eco-efficient paint shop in view of formaldehyde emissions performance, considering the results and knowledge acquired throughout this work.

Chapter 1 presented the hypothesis regarding the areas and processes of the vehicle painting operations from which emissions into the atmosphere of formaldehyde can be expected. This hypothesis is based on the evaluation of paints and materials used and the knowledge acquired from paint shop specialists and paint manufacturers, and states that formaldehyde is emitted in negligible concentrations in the waste gas coming from the spray booths but in concentrations higher than the legally applicable emission limit value in the waste gas from the drying ovens. This is due to the release of formaldehyde when the melamine formaldehyde structure is broken during the paint curing process at high temperatures. If this

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theory is confirmed, two different abatement technologies can be considered, which were also described in chapter 1.

Chapter 2 described the measurements of formaldehyde carried out at the six vehicle paint shops of the company and provided a discussion of the results in view of the hypothesis stated in chapter 1. The main areas and sources of formaldehyde emissions were identified and a proposal for corrective actions in the sources with high concentrations of this substance was given.

The concentrations observed at the waste gas from the spray booths in all paint shops were typically below 0.5 mg/m3. These values are well below the applicable emission limit value of 2 mg/m3 and confirm that the emissions from spray booths are not a concern from the legal viewpoint. On the contrary, the concentrations found at the exit of the drying ovens significantly exceed the emission limit value, with results that reach 88.3 mg/m3. These results confirm and validate the hypothesis posed in chapter 1.

Furthermore, the results obtained in chapter 2 also confirm that the high concentrations of formaldehyde after the oven can be successfully reduced to values typically below 1 mg/m3, and thus ensure compliance with the applicable emission limit value, if abatement equipment is installed to treat the waste gas from the oven and it is operated at its design abatement efficiency. In this regard, both RTO and recuperative thermal oxidizers were able to reduce formaldehyde achieving similar results. The measurements conducted at different temperatures demonstrated that a proper reduction of formaldehyde could only be achieved at abatement temperatures higher than 700 ºC. In addition, a deterioration of the desired abatement efficiency that led to high concentrations of formaldehyde could be observed when the abatement installation had damaged or old parts that needed to be repaired or exchanged.

Considering the results and knowledge gathered in chapter 2, proposals for actions to reduce the formaldehyde emissions were made for two paint shops where high concentrations were observed. These actions mainly included the increase of the abatement temperature from 540 °C to 730 °C in the primer oven abatement systems, the redirection of the primer flash off waste gas to be treated in these abatement installations, the repair or exchange of damaged parts and old abatement equipment to achieve a proper destruction efficiency, and the installation of abatement equipment at the topcoat ovens whose waste gas was emitted to the atmosphere without treatment.

These actions cannot be executed without evaluating their environmental and economic impact. Particularly, in the selection of the most suitable abatement technology for the topcoat oven emissions, the impact of the two possible technologies must be taken into account from a life cycle and an eco-efficiency perspective in order to search for the most sustainable treatment method and take it into account in the decision-making process. This evaluation was conducted and described in chapters 3 and 4. The measurement results obtained in the affected paint shop were used as input to elaborate the inventory for these assessments.

Chapter 3 dealt with the LCA of the vehicle painting process of paint shop 3. This assessment was performed to analyze the environmental impacts of the process and to compare these impacts before and after the introduction of the different actions to reduce formaldehyde emissions in the affected areas identified in chapter 2. Regarding the two topcoat oven abatement technologies evaluated, the LCA allowed the identification of the most environmentally sustainable alternative.

As an initial step, a Life Cycle Impact Assessment (LCIA) of the overall painting process in the original situation of the paint shop of study was carried out. Analyzing the hot spots, it could be concluded that the topcoat process causes the highest environmental impacts. This result was explained by the significant consumption of materials and production of emissions of this sub-process, the higher consumption of natural gas, and the direct emissions without installed abatement systems. Additionally, the electrocoating was also identified as a process with a relevant contribution to the total environmental impact, mainly due to the epoxy resin contained in the cationic paste used in this process. Improvements in the production of paints and materials, and their constituents itself, should be further pursued by paint manufacturers to reduce the environmental burdens of vehicle paints shops.

Once the overall painting process was analyzed, various improvement scenarios were evaluated, each of them corresponding to the different actions proposed to reduce the formaldehyde emissions in the paint shop. Firstly, a scenario (Scenario A) that included the reduction of free formaldehyde in paints, the treatment of the primer flash off emissions, and the increase of the temperature of the primer oven abatement installations, was studied and compared to the original situation of the paint shop (Base Case). Comparing the results of Scenario A to the Base Case, a decrease of 7 % of the human toxicity (HT) impact category was observed in the primer process. Consequently, Scenario A achieves the pursued reduction of the human toxicity through the formaldehyde emissions reduction. However, the higher natural gas consumption of this scenario due to the increase of the abatement temperature led to an increase in almost all other impact categories.

Following the analysis of Scenario A, two further scenarios for the reduction of formaldehyde emissions from the topcoat ovens were analyzed and compared to the paint shop in Scenario A. These scenarios (Scenarios B and C) studied two different abatement technologies, i.e., regenerative thermal oxidation (RTO) and recuperative thermal oxidation, respectively. It was observed that both abatement technologies achieved a decrease in the human toxicity due to the reduction of formaldehyde emissions. However, the implementation of recuperative thermal oxidizers (Scenario C) reached a more significant human toxicity reduction than the RTO (Scenario B) (5.3 % and 1.5 % reduction of the normalized index in the HT impact category for the overall painting process, respectively). On the other hand, the recuperative thermal oxidizers achieved an overall improvement when considering the most relevant impact categories selected in this study, unlike the RTO (1 % reduction of the normalized index observed for the recuperative thermal oxidizers against 2 % increase for the RTO when considering the complete painting process). These results were explained by the higher overall energy consumption of the regenerative thermal oxidation technology. Thus, the installation of the recuperative thermal oxidizers is the most environmentally sustainable alternative.

An additional scenario to reduce the VOC and formaldehyde emissions was also analyzed (Scenario D). This included the complete treatment of the emissions from the basecoat spray booths. This scenario did not achieve a reduction of the HT impact category. The improvement in the HT caused by the reduction of VOC and formaldehyde emissions is compensated by a deterioration due to the increase of the natural gas consumption.

The results obtained in the LCA confirmed that all studied scenarios achieve the pursued reduction of the human toxicity if they are compared to the original situation of the paint shop. However, the magnitude of this reduction is different for the different scenarios. The subsequent implementation of Scenario A followed by Scenario C represents the most environmentally sustainable option in view of both human toxicity and the total environmental impact. Nevertheless, the economic aspect has not been yet included in the evaluation of chapter 3. In order to provide the company with additional input for the decision-making and select the most suitable technology for the abatement of the topcoat oven emissions, an economic evaluation and an eco-efficiency analysis were conducted.

The economic evaluation and eco-efficiency analysis described in chapter 4 were performed to compare the two abatement options for the topcoat ovens of paint shop 3. In the economic evaluation, all cost data necessary to carry out the eco-efficiency analysis were collected, including installation, operational and maintenance costs of the two abatement systems over their lifetime. The eco-efficiency analysis demonstrated that in cases where only the reduction of the formaldehyde emissions to ensure legal compliance along with an overall improvement of the human toxicity are pursued and the costs are the main factor in the decision-making process, the RTO is the most economically favorable abatement option. The total costs for the implementation of the recuperative thermal oxidizers were 2.2 times those of the RTO (305.36 €/h and 136.85 €/h, respectively). Thus, the decision of the company to install an RTO at the topcoat ovens of paint shop 3 could be justified by these results.

Finally, in chapter 4 a proposal for the best eco-efficient paint shop in view of formaldehyde emissions performance was given. This proposal includes all the knowledge and outcomes acquired in this Ph.D. thesis and considers the installation of recuperative thermal oxidizers for the topcoat ovens as the best option to reduce the formaldehyde emissions decreasing the environmental footprint of the paint shop. The results provide new information to vehicle manufacturers and paint shop operators, facilitating the decision-making process in the selection of the most suitable abatement technology for the reduction of formaldehyde emissions. LCA and eco-efficiency analysis have been confirmed as powerful tools that can be applied during the planning and selection activities to evaluate and identify the most environmentally sustainable technology.

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PUBLICATIONS

Evaluation of abatement options to reduce formaldehyde emissions in vehicle assembly paint shops using the Life Cycle methodology

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***Cleaner Environmental Systems*.** ISSN: 2666-7894, Volume 11, 100139, 2023. https://doi.org/10.1016/j.cesys.2023.100139.

Specific contribution to the publication

Daniel Granadero performed the methodology, formal analysis, investigation, writing – original draft and visualization of this research article.

Quality indicator

The Journal Cleaner Environmental Systems currently presents an impact factor of 5 (2022 Journal Citation Reports), a Cite Score Index of 4.6 (according to Scopus, 5.05.2023) and the following positions in the different categories: quartile 1 (Q1) in “Environmental Science - miscellaneous” (40/163), quartile 2 (Q2) in “Environmental Science - Management, Monitoring, Policy and Law” (125/384), quartile 2 (Q2) in “Environmental Science - Environmental Engineering” (68/184) and quartile 3 (Q3) in “Energy - Renewable Energy, Sustainability and the Environment” (120/235).

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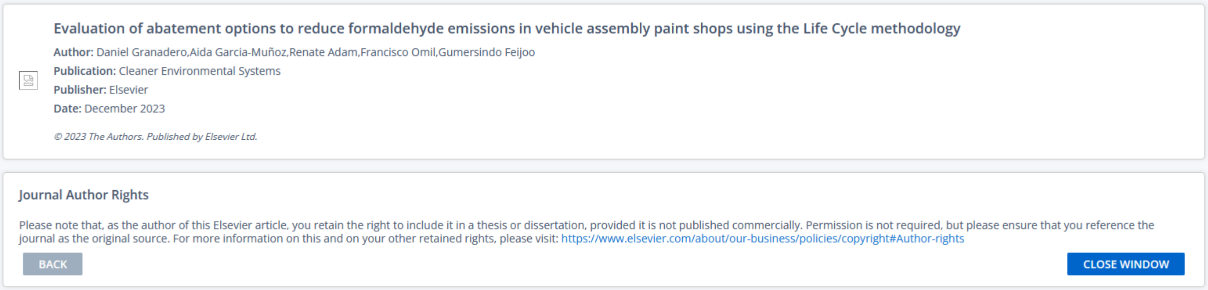

Evaluation of abatement options to reduce formaldehyde emissions in vehicle assembly paint shops using the Life Cycle methodology

Author: Daniel Granadero,Aida Garcia-Muñoz,Renate Adam,Francisco Omil,Gumersindo Feijoo

Publication: Cleaner Environmental Systems

Publisher: Elsevier

Date: December 2023

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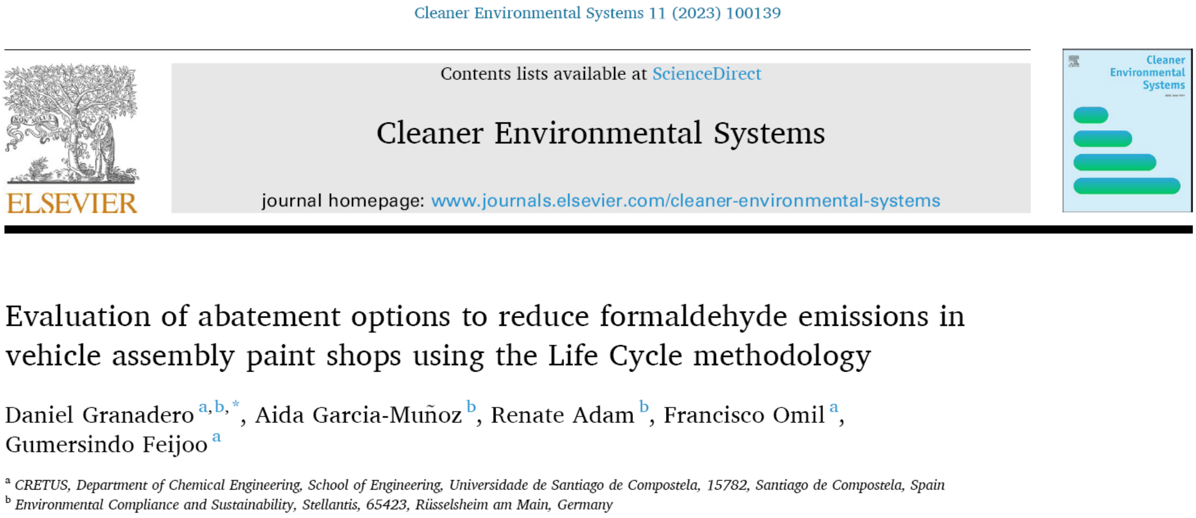

Cleaner Environmental Systems 11 (2023) 100139

Contents lists available at ScienceDirect

Cleaner Environmental Systems

journal homepage: www.journals.elsevier.com/cleaner-environmental-systems

Evaluation of abatement options to reduce formaldehyde emissions in vehicle assembly paint shops using the Life Cycle methodology

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This Ph.D. thesis assesses the impact of the change in the hazardous classification of formaldehyde in vehicle paint shops from an environmental and economic perspective. This work includes an evaluation of compliance with the applicable emission limit value for formaldehyde, a proposal of options to reduce the emissions and their economic impact, a Life Cycle Assessment of the painting process in a real vehicle paint shop and an eco-efficiency analysis. The outcomes of this thesis allowed to make a proposal for the most eco-efficient vehicle paint shop in view of formaldehyde emissions performance.