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Substitution of NMP in paint for hard PVC

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Foreword

The project “Substitution of NMP in paint for hard PVC” was funded by the Danish Environmental Protection Agency (Danish EPA) through the “Environmental Technology Development and Demonstration Program” (MUDP, under the Partnership “*Kemi i Kredsløb”*).

This report describes the project results and the methodology used in achieving these results.

In this report, a combination of letters and numbers is used to code the studied substances in the final stages of the product development, since these are considered to be of a particular confidential nature. This knowledge has been shared with the Danish EPA in confidentiality.

The project has been carried out in the period from April 2017 to May 2018 in a collaboration between Teknos, Danish Technological Institute, Research Institute of Sweden (RISE) and DHI.

To assess the progress and results of the project, a steering committee was set up consisting of the following members:

- Jens B. Ravnsbæk, R&D specialist, Teknos
- Sie W. Tordrup, Project manager, Danish Technological Institute
- Peter Kortegaard, Project manager, DHI

The progress was also followed by Dorte Bjerregaard Lerche at the Danish EPA. Dorte Bjerregaard Lerche also approved the project progress as well as the project as such and reviewed the report.

Summary and conclusion

The project purpose was to substitute N-methyl-2-pyrrolidone (NMP) in paint for hard PVC. Today, NMP is used to increase the adhesion of the paint to the PVC surface by partly dissolving the polymer. However, NMP is a substance of very high concern due to its negative effects on the human health. According to the harmonized classification of the substance it can damage the unborn child, cause severe eye irritation, cause skin irritation and cause respiratory irritation.

In this project, alternative solvents were identified and tested experimentally with respect to technical performance, assessed regarding price and commercial availability as well as evaluated with respect to exposure risk.

Main results

In order to identify alternative solvents with the desired properties, the software Hansen Solubility Parameters in Practice (HSPiP) was used. Solvents were intelligently selected for tests in the laboratories based on the theoretical calculations by the HSPiP software. The software is considered a valuable tool for identifying alternative solvents since it speeds up the substitution process and reduces the work effort involved in a typical trial-and-error based approach.

In total, three solvents (denoted S2, S3 and S7) showed excellent technical performance and are considered applicable as alternatives to NMP in PVC paint. Exposure calculations show no risk regarding environmental exposure for all evaluated alternatives, while some risk is expected with respect to dermal exposure and inhalation. The risks can, however, be controlled using proper personal protection equipment. From an exposure point of view, the solvent S2 is the preferred alternative to NMP showing lower risk both with respect to inhalation and to dermal exposure. However, this solvent has a limited commercial availability and a higher price than both NMP and the other two alternatives S3 and S7 that show similar technical performance.

Five solvent mixtures designed using HSPiP were also tested for their technical performance in paint. Only one mixture, denoted M4, passed the performance tests, whereas all other mixtures resulted in unacceptable physical changes. M4 did however, contain a substance, which is evaluated to be not readily degradable and that even at low dermal exposure levels is absorbed easily through the skin, which in this case is unpleasant for the user and therefor considered unacceptable from a user perspective.

Teknos is currently working on bringing the positive results with the solvents S2, S3 and S7 to the market in a new NMP-free PVC paint. The next step in this process is to document the long-term performance of the final product, which includes an accelerated weathering test over a longer time period.

Sammenfatning og konklusion

Projektets formål er at erstatte N-methyl-2-pyrrolidon (NMP) i maling til hård PVC. I dag anvendes NMP til at forbedre malingens vedhæftning til PVC-overfladen ved delvis at opløse polymeren. NMP er dog et særligt problematisk stof på grund af negative virkninger på menneskers sundhed. Ifølge den harmoniserede klassificering af stoffet kan det skade det ufødte barn, forårsage alvorlig øjenirritation, forårsage hudirritation og irritation af åndedrætsorganerne.

I dette projekt blev alternative opløsningsmidler identificeret og testet eksperimentelt med hensyn til teknisk præstation, vurderet med hensyn til pris og kommerciel tilgængelighed samt evalueret med hensyn til eksponeringsrisiko.

Primære resultater
For at identificere alternative opløsningsmidler med de ønskede egenskaber blev softwaren Hansen Solubility Parameters in Practice ("HSPiP") anvendt. Ved anvendelse af HSPiP blev opløsningsmidler udvalgt intelligent til test i laboratorierne baseret på teoretiske beregninger af softwaren. Softwaren betragtes som et værdifuldt værktøj til at identificere alternative opløsningsmidler, da det fremskynder processen og reducerer den arbejdsmæssige indsats, der er involveret i den typiske prøv-og-fejlbaserede tilgang.

I alt viste tre opløsningsmidler (S2, S3 og S7) fremragende teknisk egenskaber og betragtes som anvendelige alternativer til NMP i PVC-maling. Eksponeringsberegninger viser ingen risiko for miljømæssig eksponering for alle evaluerede alternativer, mens der er risiko for hudeksponering og eksponering ved indånding, risikoen kan dog kontrolleres ved brug af passende personlige værnemidler. Ud fra et eksponeringssynspunkt er opløsningsmidlet S2 klart det foretrukne alternativ til NMP, og viser lavere risiko både med hensyn til inhalation og hudeksponering. Dette opløsningsmiddel har imidlertid en begrænset kommerciel tilgængelighed og en højere pris end både NMP og de to andre alternativer med fremragende teknisk ydelse.

Fem blandinger af opløsningsmidler designet ved hjælp af HSPiP blev også testet for deres tekniske egenskaber i maling. Kun én blanding, M4, bestod de gennemførte tests, mens alle andre blandinger resulterede i uacceptable fysiske ændringer. M4 indeholdt imidlertid et stof, som vurderes at være ikke let nedbrydeligt og som selv ved lave niveauer af hudeksponering absorberes let gennem huden, hvilket anses for uacceptabelt ud fra et brugerperspektiv.

Teknos arbejder for tiden på at bringe de positive resultater med opløsningsmidlerne S2, S3 og S7 til markedet i en ny NMP-fri PVC-maling. Det næste trin i denne proces, er at dokumentere det endelige produkts langsigtede ydeevne, som omfatter en accelereret vejrprøvning over en længere periode.

1. Introduction

1.1 NMP – a solvent added for adhesion enhancement

The compound N-methyl-2-pyrrolidone (NMP, CAS number 872-50-4) is currently used as a solvent in paint for PVC to enhance the adhesion. However, the compound has been included in the candidate list under REACH as it is classified as toxic for reproduction category 1B, the LOUS list from the Danish Environmental Protection Agency (Danish EPA) and a restriction will come into force by 2020[1] setting a limit value of 0,3 %.

According to the harmonized classification within the EU, NMP may damage the unborn child, causes serious eye irritation, skin irritation and may cause respiratory irritation.

It is estimated that in 2020 more than 3 million PVC-windows will be produced, which requires painting. With a NMP content of 5-15% (by weight) in a typical PVC-paint and a total global consumption of 600 tons, substitution of NMP in this type of product has a great potential to reduce the human exposure to the substance at a global level.

A water-based paint with an improved environmental and health profile compared to paint containing NMP will represent a significant competitive advantage for Teknos and is expected to lead to increased growth both in national and international markets. Industrial Wood in Teknos is the segment that deals with surface treatment solutions for both indoor and outdoor wood, as well as composite materials and plastic windows. Customers are already inquiring about an NMP-free product for this segment and Teknos expect the developed product without NMP to provide a better service for customers and potentially lead to an increase in market shares.

However, Teknos' previous attempts to identify alternative solvents for adhesion promotion with a better environmental and heath profile have not been successful.

Currently, Teknos use solvents that are structurally similar to NMP, such as NEP (1-ethylpyrrolidin-2-one, CAS-no. 2687-91-4) and NBP (1-butylpyrrolidin-2-one, CAS-no. 3470-98-2). NEP is currently the preferred solvent used instead of NMP, but it is not a satisfactory long-term substitution, as it also has a reproductive toxicity category 1B classification.

The current project has focused on the identification and testing of possible solvent substitution candidates. Additionally, other types of treatment, which possibly could increase adhesion have also been considered briefly (see overview in Appendix 2). A 1:1 substitution of the solvent is however easy to implement and therefor the preferred choice. Since several solvent alternatives were identified early in the project, no further work was done with other types of treatment.

This project has identified and tested a range of possible NMP substitution candidates. The candidates were selected and evaluated according to performance, health and environmental evaluations, cost and availability.

[1] COMMISSION REGULATION (EU) 2018/588 of 18 April 2018 https://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:32018R0588&from=EN

2. Framework

The project was initiated by setting up criteria for potential substitution candidates on three critical aspects: the chemical and technical requirements, health and environmental requirements and commercial aspects. The criteria were used in the evaluation and selection of potential candidates throughout the project.

2.1 Chemical and technical aspects

2.1.1 Assessment criteria for the evaluation of alternatives to NMP

The properties of alternatives to NMP should not necessarily match those of NMP exactly, but should perform similarly to NMP in the application. It is expected that the enhanced adhesion of NMP-containing paint is due to a partial dissolution of the PVC surface resulting in intermingling of the paint and PVC, see Figure 1. Therefore, an alternative solvent to NMP must be able to dissolve PVC.

The solvent should also be miscible in the formulation. The binders are responsible for the required outdoor and accelerated weathering resistance needed in the paint and hence an essential component in the formulation. It is expected that changing the binders will affect the weathering resistance, possibly decreasing it to an unacceptable level. Therefor it was decided, that only the binders that are currently used in the formulation should be used in the development work in order to secure the required properties regarding weathering resistance. Other raw materials in the formulation can be changed, if necessary, without significantly affecting the weathering resistance.

The final formulation shall comply to AAMA 615-13[2] with at least the same results as the current formulation containing NEP, since this is a general requirement from customers of Teknos.

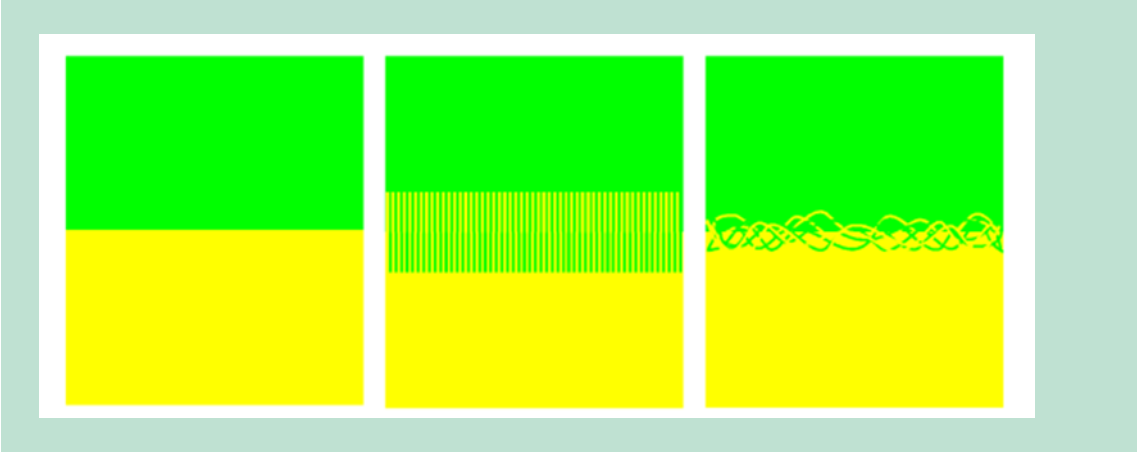

Figure 1. Figure adapted from the HSPiP[3] Manual showing different degrees of intermingling. From left: no intermingling (surface energy only, poor adhesion), straight intermingling (“nail” adhesion), contrasted with entanglement (real adhesion).

[2] Voluntary Specification, Performance Requirements and Test Procedures for Superior Performing Organic Coatings on Plastic Profiles set by the American Architectural Manufacturers Association.

[3] Hansen Solubility Parameters in Practice – Software to predict solubility of components in a formulation - https://www.hansen-solubility.com/HSPiP/

2.2 Economic aspects

The cost of alternative solvents to NMP and other costs related to substitution will be considered during the development work and compared to costs associated with the use of NMP and NEP. The amount of NEP in the current formulation is approximately 1-15 % (w/w). Depending on the required amount of substituted/alternative solvent, the price of the product containing the NEP alternative shall preferably not exceed the total raw material cost price of the NEP-containing product. This means, that if an alternative is more expensive, this will increase raw material cost for the solvent, but the increase in total cost of raw material might be insignificant if the solvent proves more efficient and therefor can be used at a lower concentration.

2.3 Health and environmental aspects

The alternative should meet several criteria regarding the environment and human health. In order to ensure that the substitute is a good alternative for NMP – it should be less problematic when considering human health and environment.

The industrial use of the product means that several measures can be controlled, e.g. waste water treatment, emission, use of closed systems etc. However, neglecting environmental and human health concerns will have a negative effect on the applicability of the new formulation, because administration, costs and environmental procedures may be challenged. Thus, a number of criteria have been defined, which the alternative solvent and final product should meet. These criteria together with the applied assessment methods are summarized in **Table 1**.

Table 1 refers to the below assessment methods:

- EPI Suite: A suite of QSAR models for predicting physical-chemical, ecotoxicity and fate data of chemical substances. It can freely be downloaded from: https://www.epa.gov/tsca-screening-tools/download-epi-suitetm-estimation-program-interface-v411
- VEGA: A suite of QSAR models to predict toxicity, ecotoxicity, environmental and physical-chemical properties of chemical substances. It can freely be downloaded from: https://www.vegahub.eu/download/
- Danish (Q)SAR Database: is a database contained QSAR predicted properties (human and environmental toxicity, physical-chemical and fate properties of chemical substance. It is developed at Division of Diet, Disease Prevention and Toxicology, National Food Institute, Technical University of Denmark, http://qsar.food.dtu.dk.

Table 1. Environmental and human health hazard criteria, which the alternatives must meet. Please refer to the list of abbreviations for further explanation (Appendix 1)

Criteria	Specification	Criteria	Assessment method
SVHC-properties			
PBT		Not acceptable	Data retrieval supported by QSAR / EPI Suite calculations
vPvB		Not acceptable	Data retrieval supported by QSAR / EPI Suite calculations
CMR	Carc. 1A Carc. 1B Muta. 1A Muta. 1B Repr. 1A Repr. 1B	Not acceptable	Lookup in ECHAs CLP Inventory Database. If sufficient data for assessing the CMR classification is not available, a combination of data search, read-across and QSAR calculations are used.
Endocrine disruptor	Known endocrine	Not acceptable	Lookup in Endocrine Disrupter

Criteria	Specification	Criteria	Assessment method
	disruptor		priority list[4] QSAR screening for ED properties (VEGA, Danish (Q)SAR Database)
Classification			
Env. Class. (PBT/vPvB)	Aquatic Acute 1 (H400) Aquatic Chronic 1 (H410) Aquatic Chronic 2 (H411)	Preferably, the substitute is not classified for environmental hazard. However - if classified - acceptance depends on category, M factor etc.	Data retrieval supported by Lookup in ECHAs CLP Inventory database and QSAR / EPI Suite calculations.
Acute Tox.	Acute Tox. 1 Acute Tox. 2 Acute Tox. 3	Preferably, the substitute is not classified with Acute Tox. 1-3. However, if the classification of the formulation is not Acute Tox. 1-3, this is considered acceptable[5].	Lookup in ECHAs CLP Inventory. If sufficient data for assessing the Acute classification is not available, a combination of data search, read-across and QSAR calculations are used.
VOC		Non-VOC alternatives preferred. Overall, the VOC of the product should be as low as possible.	Boiling point and vapor pressure is used for VOC classification. These data are retrieved through data collection and – if needed - estimation using modelling (EPI Suite).
Odor	Smell nuisance	Not preferred	
Dangerous Goods	Product transport classification.	Final product is preferably not classified as dangerous goods (DG), but depending on class and packaging group (PG) this may be acceptable. It costs extra to ship DG plus UN approved packaging.	

[4] Study on enhancing the Endocrine Disrupter priority list with a focus on low production volume chemicals, http://ec.europa.eu/environment/chemicals/endocrine/pdf/final_report_2007.pdf

[5] In many countries, a product classified as Acute Tox. 1-3 faces restrictions in sales and applications.

3. Solvent screening – identification of possible alternatives

A list of solvents, capable of substituting NMP and NEP, were identified through a screening process. Using several tools, the physical, chemical, health and environmental properties of the solvents were evaluated and the list reduced based on these parameters until only the best and most promising alternatives were left for further product development.

3.1 Screening using the Hansen Solubility Parameter in Practise program

Hansen's Solubility Parameters in Practice (HSPiP) was used and proved to be a strong tool for identifying possible NMP/NEP alternatives. The 'Hansen-tool' is one of the tools described on Kemi i Kredsløbs webpage,[6] and is a theoretical tool to identify an alternative solvent or solvent combinations that can dissolve a specific polymer. By determining the solubility parameters of PVC, HSPiP was used to prepare an initial list of possible alternative solvents, theoretically capable of dissolving PVC. Two types of PVC materials used by Teknos in their paint tests were used to determine the specific solubility parameters through swelling tests. The two types were selected because they represent commonly used PVC types in EU and the United States, respectively, and vary in the content of e.g. additives used. These differences in chemical composition have an influence on the processing parameters of the PVC, but it is uncertain if they affect the solubility parameters as well,

3.1.1 Method for determining solubility parameters

The first step in using the HSPiP tool is to determine the Hansen Solubility Parameters for the two types of PVC, which was carried out as described in the following. PVC pieces where grinded to approx. 1 mm granules. Grinded PVC (0.2 grams) was placed in 2 mL solvent and evaluated after 24 hours. Solvent performance was rated between zero (no interactions with the granules) and one (swollen granules). In total, 14 different solvents were used to examine the swelling or dissolution of the two PVC materials. The 14 solvents chosen represents solvents with a wide range of solubility parameters. The ratings of each of the solvents were fed into the HSPiP program. The program output is a set of three Hansen parameters (H, D and P) for the PVCs, each of which represents a dimension in a 3-dimensional coordinate system referred to as the 'Hansen space', see the illustration in Figure 2.

3.1.2 Hansen Solubility Parameter results and discussion

Swelling/dissolution differences between the two PVC materials were not observed by the visual evaluation of the interactions with the 14 solvents used for the test. Consequently, the HSP of these two materials are very similar and regarded as indistinguishable for this project. Since the two PVC types tested are expected to represent the PVC that differ most remarkably within the common types known to Teknos, it is expected, that a match of the HSP of these PVC types will be a match for other common PVC types.

From these experiments, the following parameters were found for the PVC materials in the HSPiP program: D= 19.0 P=10.2 H=7.5. The radius was found to be 6.8, and the sphere is shown in Figure 2.

[6] http://web.kemiikredsloeb.com/mod/lesson/view.php?id=408&pageid=95

The figure shows how the PVC result is illustrated in the HSPiP software. The PVC parameters are plotted as the center of the green sphere in the “Hansen space”. The three solubility parameters (D, P, H) are used as axes. Blue dots indicate a good solvent match, while red boxes indicate poor solvents – NMP is plotted in yellow for comparison.

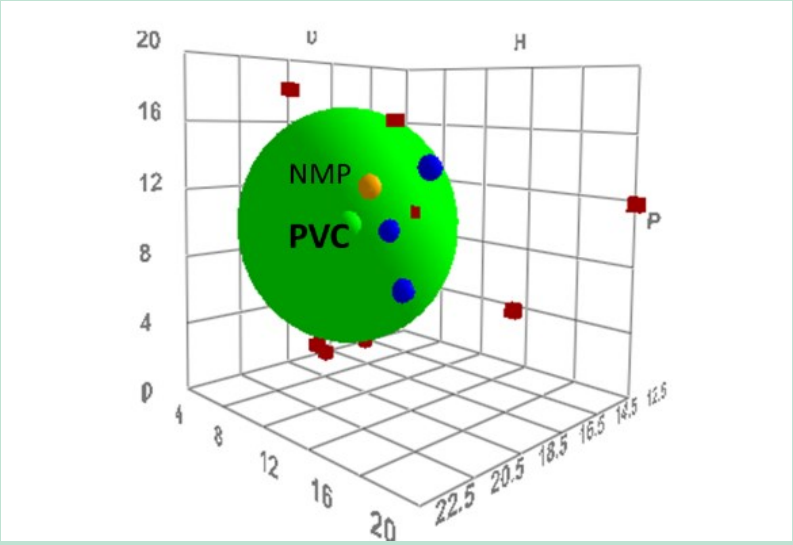

Figure 2. Illustration of the PVC sphere from the HSPiP tool with the solubility parameters H, D and P as the X, Y and Z axis.

Using the “green solvent list”[7] available via the HSPiP software, 21 solvents were identified as possible alternatives to NMP, since they fall within the radius of the PVC sphere. The solvents are listed in **Table 2**. The list was scrutinized against relative evaporation rates (RER) below 10 to ensure sufficiently low evaporation rates and a radius of the sphere, i.e. the distance to the PVC center below 4. An initial evaluation of the solvents falling within this radius regarding health and environmental effects (based on criteria setup in **Table 1**, see section 3.2), commercial availability and price was performed. Each parameter was given a color (red-yellow-green) to give an overview of the overall evaluation of the identified alternative solvents. In **Table 2**, information on the price parameter has been omitted due to its sensitive nature. If necessary, the identified solvents found in the screening can also be used as mixtures to improve the solubility properties. This could be beneficial if two given solvents are on opposing sides of the PVC sphere.

Table 2. List of the alternatives for NMP found by HSPiP using solubility parameters of PVC and the HSPiP green solvent list. The parameters are categorized into three colors. For the environmental and toxicology parameter, the colors indicate - Red: Not a useable substitution due to SVHC properties, Yellow: Certain amount of risk – DHI needs to look into the toxicological data. Green: Without any worrying health and environmental aspects observed in initial

[7] The green solvent list was created by researchers (Prof. Aubry and Prof. Clark) with the intention to rank solvents from a Safety, Health and Environment perspective, aligned with the Global Harmonized System (GHS) and European regulations. It is a list of environmentally friendly solvents originating from the processing of agricultural crops.

screening. The commercial parameter - Red: Not available, Yellow: Should be available. Green: Good availability at the three suppliers contacted by Teknos.

Name	CAS number	Environment. & toxicology (initial screening)	Commercial availability
Dimethyl isosorbide	5306-85-4		
1,3 – dioxolane	646-06-0		
Gamma-valerolactone	108-29-2		
Furfural	98-01-1		
Methyl 5-(Dimethylamino)-5-Oxopentanoate	14471-87-5		
Dimethyl 2-methylglutarate	19013-37-7		
N,N - dimethyldecanamide	14433-76-2		
benzyl benzoate	120-51-4		
Glycofurol (N=2)	31692-85-0		
Tetrahydrofurfuryl alcohol	97-99-4		
N,N - dimethyloctanamide	1118-92-9		
Anisole	100-66-3		
Diethyl glutarate	818-38-2		
Dimethyl glutarate*	1119-40-0		
Dimethyl adipate*	627-93-0		
Dimethyl succinate*	106-65-0		
Diethyl adipate	141-28-6		
MEK / butanone	78-93-3		
Gamma-butyrolactone	96-48-0		
Diethyl succinate	123-25-1		
Polar Clean	1174627-68-9		

***commercially sold as a mixture of dimethyl glutarate, adipate and succinate, known as dibasic esters.**

3.2 Screening of health and environment effects

The initial screening of environmental and human health hazards (an initial SVHC-screening based on classification and check if the substance is found on the candidate or authorization list or is restricted) excluded several substances meeting the criteria regarding compatibility with PVC (see previous section 3.1).

The substances which were characterized as having good commercial availability (green color in **Table 2**) together with a human health and environmental hazard showing no apparent concern (green color in **Table 2** – therefore named “green substances”) were then assessed in more detail using the methods described in 2.3. More substances were added to the health and environmental evaluation for use either as “stand-alone” solvents or for use in mixtures, namely: Dimethyl 2-methyl gluterate, DMSO, Ethyl acetate and Ethyl lactate (see section 4.1 for details). Two of these are, due to their solubility properties tested as single solvent alternatives and two are used in mixtures only.
The assessment of these substances is described in section 3.2.1.

The substances which were characterized as having good commercial availability (green color in **Table 2**) together with a human health and environmental hazard, which could not be concluded on the basis of the initial screening (yellow color in **Table 2** – therefore named "yellow substances") were then assessed in more detail using the methods described in 2.3. This is described in section 3.2.2.

3.2.1 Screening of green substances

A human health and environmental screening according to section 2.3 of the below substances was carried out:

I. Loxanol
II. γ-butyrolactone
III. Cyrene ((1S,5R)-6,8-dioxabicyclo[3,2,1]octan-4-one)
IV. Benzylbenzoate
V. DBE: Dibasic esters: mixture of:
    a. Dimethyl glutarate
    b. Dimethyl adipate
    c. Dimethyl succinate
VI. Dimethyl 2-methylglutarate (added as additional optional alternative)
VII. DMSO (added as additional optional alternative)
VIII. Ethyl acetate (added as additional optional alternative)
IX. Ethyl lactate (added as additional optional alternative)

Results for these substances are reported in Appendix 3.2.

3.2.2 Screening of yellow-substances

According to section 2.3, a human health and environmental screening of one substance was carried out:

- 1,3 – dioxolane (CAS: 646-06-0)

3.2.2.1 Dioxalane

The substance is not found to be either a PBT nor a vPvB substance.

The harmonized classification for 1,3 – dioxalane does not include any CMR-classification phrases. The classification in the REACH registration dossier does not include CMR classification phrases (with sufficient data for assessing the classification). However, the substance is on the CoRAP[8] list as it is suspected for being toxic to reproduction and to show mutagenic toxicity. Read-across to 1,4 dioxane (which is classified as carcinogenic) may indicate carcinogenic properties.

It cannot be excluded that the substance may have CMR-properties. Therefore, it is recommended not to use this substance for substitution of NMP. Any considerations on using the substance should await the conclusions from CoRAP.

For further details on screening, see Appendix 3.1.

[8] The Community rolling action plan (CoRAP) indicates substances for evaluation by the Member States in the next three years and is updated each year in March. The evaluation aims to clarify the initial concern that the manufacture and/or use of these substances could pose a risk to human health or the environment.

3.3 Conclusion

HSPiP provided 21 possible alternatives, which were initially screened with respect to availability, environment and toxicology. It was decided not to include 1,3 – dioxolane, as it currently cannot be excluded that the substance has CMR-properties. Based on the initial theoretical evaluation, a selection of nine solvents were selected for further tests and health/environmental evaluation, either as stand-alone solvents or as mixtures for possible NMP or NEP substitution.

The nine solvents are due to confidential information randomly named using a coding of S1 to S9. A further investigation of these substances with respect to technical performance and health and environment was performed in the project and the results are described in the following paragraphs.

4. Performance test and health and environmental assessment

A selection of possible alternatives was added to a base paint formulation and screened for their performance in a series of representative tests. The performance results compared to that of paint containing NEP.

4.1 Introduction to performance testing

A list of nine possible solvent alternatives, which were initially identified by theoretical measures (e.g. HSPiP, green solvent list, chemical and physical, environmental and health properties), were screened primarily for their performance, still taking health, environment and availability into the consideration.

The alternative solvents were formulated as a direct 1:1 NEP substitution by weight in a base paint system from Teknos, which includes relevant components such as binders, pigments, thickener, anti-foam agents and fillers, consequently bringing the results closer to "real-life" application. To evaluate wherever these new formulations exhibited the required technical performance, a selection of AAMA 615-13[9] test procedures were used:

- **Dry adhesion**; adhesion of the cured coating under dry conditions
- **Wet adhesion**; adhesion of the cured coating when exposed to water for 24 hours at 38°C prior to adhesion test.
- **Window cleaner**; visual appearance and adhesion test of the cured coating after exposure to window cleaner for 24 hours.
- **Cold crack cycle**; several repetitions of exposure to high humidity for 24 hours followed by cooling for 20 hours below 0°C and then left in room temperature for four hours.

Besides the above-mentioned tests, all formulations were evaluated according to physical and chemical stability and viscosity at relevant storage conditions and periods (accelerated tests at 40°C).

The majority of the selected solvent (S1-S7) were tested as single solvents and the single solvent tests have been top priority during the development work. Substitution with a single solvent is the easiest way to substitute, if it is possible to find an alternative that performs adequately. Mixing of solvents makes it possible to match the specific solubility parameters of PVC using two or more solvents which on their own do not match the solubility properties closely. Only a few mixtures (M) have been tested and these have been based on solvents S3, S5 and S6 (close match in solubility parameters and tested as single solvents) as well solvent S8 and S9 (not a close match in solubility parameters but in combination with solvents S3, S5 and S6 they became relevant for mixtures).

4.1.1 Performance tests for single solvents – results and discussion

The results of the four selected performance tests are summarized in **Table 3.**
NEP, the current benchmark at Teknos, is included for comparison along with a base paint without solvent (negative reference).

[9] Voluntary Specification, Performance Requirements and Test Procedures for Superior Performing Organic Coatings on Plastic Profiles set by the American Architectural Manufacturers Association.

Table 3. Results of the selected tests on paint containing NEP and the chosen alternatives. Green indicates good performance, yellow indicates acceptable performance, red indicates unacceptable performance. NA denotes that results are not available.

Solvent	Single solvent or mixture	Adhesion, dry	Adhesion, wet	Window cleaner	Cold crack	Viscosity change	Note
None[10]	*Not relevant*						
NEP[11]	Single						
S1	Single						Visuals appearance alters during cold-crack cycles.
S2	Single						
S3	Mixture						
S4	Single						Visuals appearance during cold-crack cycle unacceptable
S5	Single	NA	NA	NA	NA	NA	Not received for testing.
S6	Single						Visuals appearance alters during cold-crack cycles.
S7	Single						

The negative reference (no solvent, denoted 'None' in **Table 3**), unexpectedly exhibited good results in the dry and wet adhesion test as well as in the cold crack test. On the other hand, the negative reference coating cannot withstand window cleaner, proving the need for a solvent in the formulation. S4 fails in both the window cleaner test and the cold crack test and is therefore considered an unacceptable alternative. S1 and S6 pass all respective conducted tests, even though some alteration in the visual appearance was observed during the cold crack test (denoted by yellow color, **Table 3**). Despite the changes in visual appearance of formulations with S1 and S6, these are not excluded because the alterations are only minor and do not seem to decrease the performance of the coating. Currently, S1 is still early in the commercial development as a solvent for industrial use, and is thus of reduced availability. The limited availability of S1 could prove to be a problem, as both price and ready availability are necessary for a successful implementation of the alternative. S6 is easily adsorbed through skin even at low dermal exposure levels, which is unpleasant for the user and therefor considered unacceptable from a user perspective. S5 was not received in time for testing as a single solvent, but only used in later experiments in mixtures with other solvents. Additionally, S5 is a precursor and prodrug for a substance, which is a known neurotransmitter and psychoactive drug. However, there does not seem to be any regulations, restrictions or registration issues related to the use of S5, thus S5 is still considered a suitable alternative for NEP.

[10] Negative reference; formulation containing no adhesion promoting solvent

[11] Positive reference; formulation containing the benchmark solvent at Teknos today.

4.1.2 Performance test for mixtures – results and discussion

Mixtures of the different solvents were only tested in formulation to a very limited extent in this project due to the positive results of single solvent alternatives. Initial tests with mixing S3 with other alternatives showed problems related to unpredictable viscosity changes during storage, possibly making shelf-life unpredictable. As a standalone solvent, these problems were not observed. Due to the acceptable to good performance of several single substance alternatives only five mixtures were evaluated during the development. The mixtures contain some of the solvents used as single solvents as well as two additional solvents (S8 and S9), that do not match the PVC solubility parameters close enough to act as single solvent alternatives. However, when used in combination with other solvents, solubility parameters of the resulting mixtures will match the PVC solubility parameters.

The five mixtures were chosen using the Hansen's solubility program. Each mixture was chosen for having solubility parameters similar to PVC and consists of two solvents from the green solvent list in different ratios. The mixtures are shown in **Table 4** along with the results of the evaluations made.

Table 4. Results from the initial performance tests of the solvent mixtures

Code	Mixture contains	Adhesion, dry	Adhesion, wet	Window cleaner	Viscosity change over 7 days
M1	S3+S5				
M2	S5+S9				
M3	S6+S9				
M4	S3+S6*				
M5	S5+S8				

*Mixture contains S6, which is easily absorbed through human skin, which can be unpleasant for the user even at low exposure.

4.1.3 Conclusion

S4 is no longer considered a possible alternative due to the unacceptable technical performance observed in the performance tests. For all the remaining single substance alternatives, a more extensive health and environmental evaluation was now performed, with both S1 and S6 on the "observation list" due to the observed but acceptable changes during cold crack testing. Substances used only in the mixtures (S5, S8 and S9) was included in the health and environmental evaluation.

4.2 Health and environmental evaluation

The human health and environmental evaluation of the alternatives (S1 – S9) is shortly described in section **Fejl! Henvisningskilde ikke fundet.** and in further details in Fejl! Henvisningskilde ikke fundet.. The overall conclusion is that none of the alternatives should be excluded due to their human health and environmental properties. Furthermore, it is not possible to prioritize the alternatives from the screening results, except for that S4 may be a slightly less attractive alternative due to its environmental classification and classification under transport regulation. In addition, S6 is found to be not readily biodegradable and the substance easily adsorbs through skin even at low dermal exposure, which in this case is unpleasant for the user and therefor considered unacceptable.

4.2.1 Human health and environmental risk assessment of the alternatives

Another way of assessing the human health and environmental impact is to make a safety assessment of the alternatives – considering the actual exposure through identified uses and activities. This has been prepared in a separate confidential report (not included here), and only the main results are presented here.

A safety assessment of the use of NMP (and its alternatives) has been prepared both during paint production and the downstream use at the windows-manufacturer, where the paint is applied.

Thus, exposure and safety assessment is performed both for paint containing the NMP and paint containing one of the alternatives. The safety assessment is based on the inherent properties of the substance and the use conditions. It is assumed that the alternatives will be present at the same concentration in the paint as NMP.

Substances used as single solvents (S) as well as mixtures of substances (M) were included in the assessment.

In terms of human exposure, both occupational exposure via inhalation and dermal exposure are considered. The paint applied to the windows is expected to be completely hardened, so no residue of the solvent is expected to be present at the point where the coated window frames are marketed, which means that no service life considerations are necessary.

Substance profile

Several substance parameters are needed for the exposure and safety assessment. These are presented in a confidential report.

Use data

The use data are obtained from the use mapping that CEPE[12] has carried out and are believed to be relevant to 80% of the paint applications in industry. The use mapping from CEPE was shortened by Teknos, so only uses considered relevant to the product is included in the following development work. The use mapping includes 16 activities in the formulation (manufacture) of the paint at Teknos and 25 activities in the industrial end-use of the paint, see Appendix 4 for further description of each use.

[12] CEPE is the European Council of the Paint, Printing Ink and Artists' Colours Industry

Exposure and safety calculations

For this screening ECETOC TRA[13] (workers, inhalation, dermal) was used for occupational exposure calculations. Exposure was calculated without considering Personal Protection Equipment (PPE), but ventilation and Local Exhaust Ventilation were considered. It should be emphasized that both manufacture and use of the paint is handled by professionals only, so all required PPEs (dermal and inhalation) are expected to be applied. The defaults of ECETOC TRA were used in the calculations.

EUSES[14] is used for environmental calculations. According to provided information, waste water from Teknos is handled by flocculation before final discharge to sewer. However, it is assessed that neither NMP nor the considered alternatives will be removed to any major degree by this process. The following settings were used for the environmental exposure calculations (Table 5).

Table 5. Settings for the environmental exposure calculations

Life cycle stage	ERC	Assumed fraction discharged to waste water	Volume of paint[15]	Concentration of solvent (amount in produced paint) (NMP)	Number of production days
Manufacture at Teknos	ERC 2	0.0216	75000 L/yr	5% (3750 L/yr)	225 d/yr
End-use of NMP (or alternative) in paint – largest customer	ERC 4	0.0217	50000 L/yr	5% (2500 L/yr	225 d/yr

In addition, the Risk Characterization Ratio (RCR) is calculated for all activities and substances. The RCR is calculated by dividing the exposure concentration by a zero-effect-concentration (DNEL (Derived No Effect Level) for human safety assessment; PNEC[18] (Predicted No Effect Concentration) for environmental safety assessment).

A RCR above 1 for dermal or inhalational exposure indicates that PPE is most likely needed in order to ensure safe use. Likewise, a RCR above 1 for the environment indicates that releases to the waste water need to be reduced. The calculated RCR values are presented in the next chapter.

4.2.1.1 Exposure and safety assessment for exposure via inhalation

Fejl! Henvisningskilde ikke fundet. shows the calculated RCR (inhalation) for the various uses of each assessed solvent (S) and solvent mixture (M). Uses 1-16 cover the manufacture activities and uses 17-41 cover the industrial end-use phase (see Appendix 4).

[13] ECETOC TRA is a tool for Targeted Risk Assessment from European Centre For Ecotoxicology and toxicology of Chemicals. It is here used for calculating the workers dermal and inhalational exposure to the substance

[14] The European Union System for the Evaluation of Substances. This is a model for predicting environmental concentrations on the basis of release pattern and substance fate properties.

[15] Information from Teknos

[16] Conservatively based on the ERC 2

[17] CEPE SPERC 4.1b.v1 (application - industrial - spraying - indoor use - volatiles)

[18] The PNEC is derived by dividing the lowest effect concentration by an assessment factor (AF). The better data set the lower assessment factor is used.

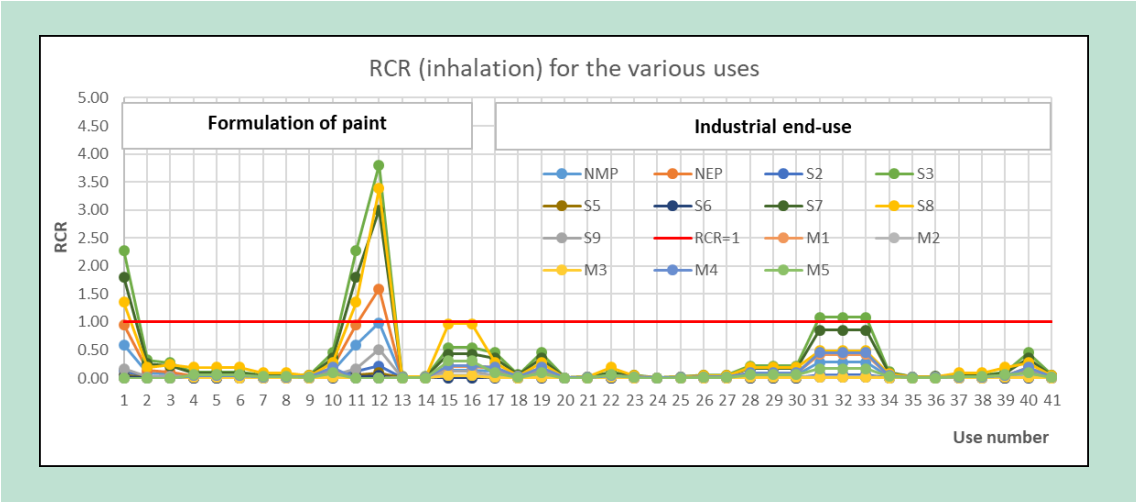

Figure 3. Calculated RCRs for exposure via inhalation. Use 1 – 16: Formulation of paint (at Teknos). Use 17-41: Industrial end-use of paints. For use description see **Appendix 4.**

It is observed that the RCRs in general are higher for the formulation phase than the end-use phase – thus requiring higher degree of inhalational protection.

Looking at the RCR(inhalation) then the general sorting order is (compounds with the same color has the approximate same level of RCRs):

S3 > S8 > S7 > NEP > NMP > S9 > M4 > M1 > M5 > S2 > S5 >M2 >M3 > S6

The red formatting color indicates the highest RCRs and the green color indicates the lowest RCRs, but the color does not indicate whether or not the corresponding RCR is above or below 1.

S1 is not included in these observations as no DNEL was available for this substance. Due to lack of data it was not possible to derive a DNEL for this substance within the scope of this project.

Thus, S3, S7 and S8 tend to have the highest RCRs when looking at exposure via inhalation. S6 has the lowest RCRs (inhalation). RCRs for NMP are all below 1 for inhalation risk for the various uses.

The best option based on the calculated RCRs for human exposure via inhalation appears to be S6, followed by S5 (not received in time for performance testing) and S2. These substances appear also to result in lower RCRs than NMP. NEP, S8, S3 and S7 appears to result in higher RCRs than NMP.

Looking at the formulation phase, the highest RCR(inhalation) of approximately 4 is noted for S3 at use A12. This requires a PPE with an efficiency of approximately 80% in order to ensure safe use.

Looking at the end-use phase, the highest RCR(inhalation) of approximately 1.1 is noted for S3 at uses B15, B16, B17. This requires a PPE with an efficiency of approximately 10-20% in order to ensure safe use.

The mixtures M1, M2, M3, M4, M5 appear to have RCRs below 1, so the exposure via inhalation to the mixtures are not expected to exhibit a risk to workers.

4.2.1.2 Dermal exposure and safety assessment

Figure 4 shows a comparison of the calculated RCRs (dermal) for the considered substances (S) and mixtures (M). The relative ratios of RCRs do not vary for the various activities when looking at dermal exposure, so the ratios are the same for all identified uses.

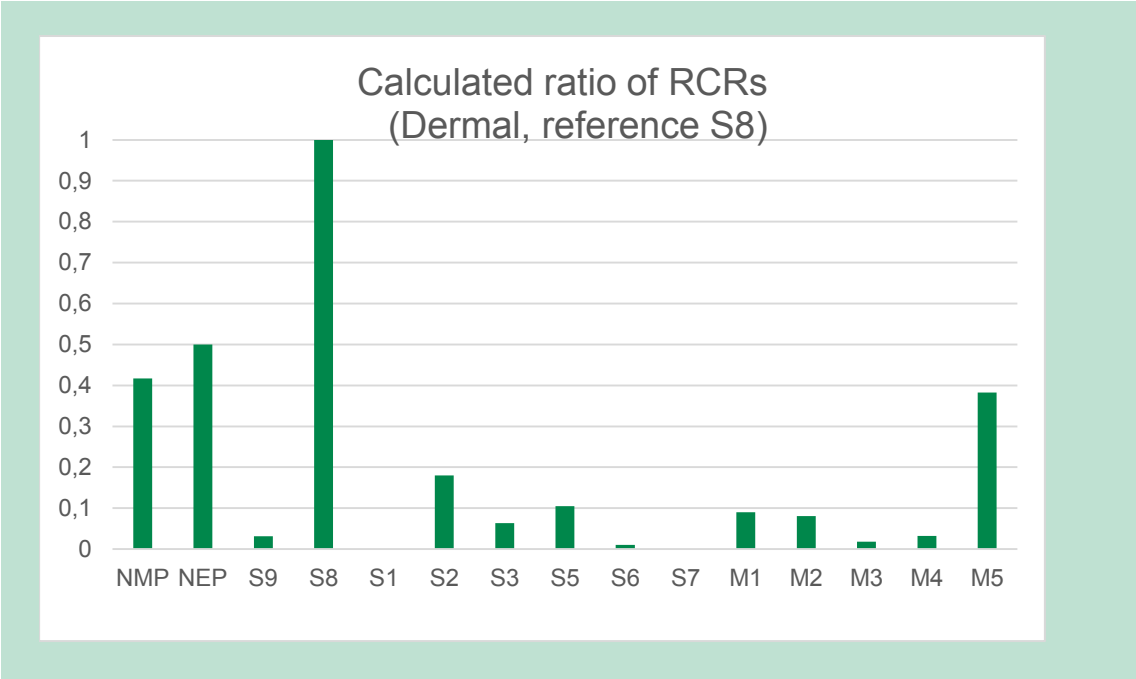

Figure 4. Ratios between calculated RCRs for dermal exposure (S8 set as reference). The relative ratios of RCRs do not vary for the various uses when looking at dermal exposure.

Figure 5 shows the calculated RCR (dermal) for the various uses. It is seen that in general the RCRs are higher for the formulation phase than the end-use phase, thus requiring higher degree of dermal protection.

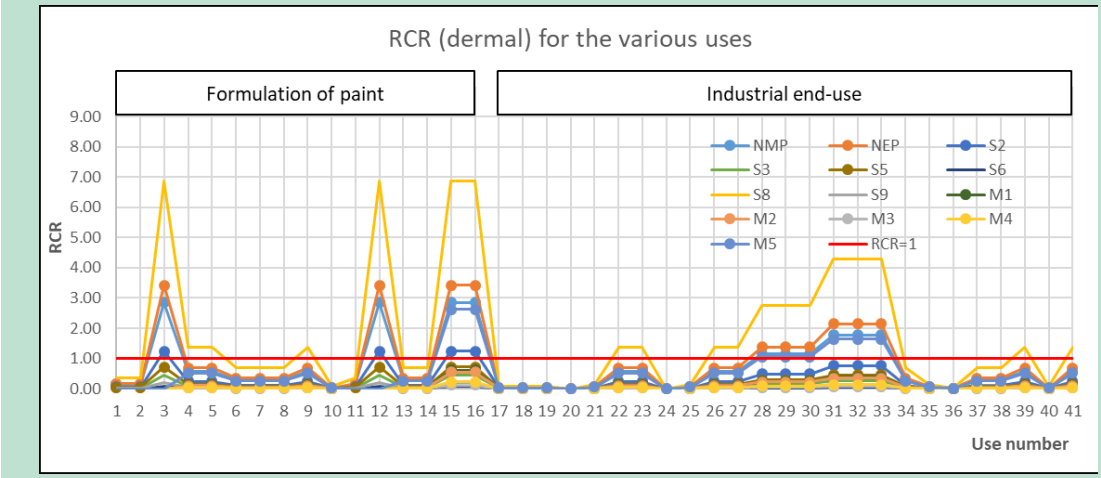

Figure 5. Calculated RCRs for dermal exposure. Use 1 – 16: Formulation of paint. Use 17-41: Industrial end-use of paints. For use description see **Appendix 4.**

Looking at the RCR(dermal) then the general sorting order is (compounds with the same color has the approximate same level of RCRs):

S8 > NEP > NMP > M5 > S2 >S5 >M1 > M2 > S3 > M4 > S9 > M3> S6

As explained in the previous section, the red formatting color indicates the highest RCRs and the green color indicates the lowest RCRs, but the color does not indicate whether or not the corresponding RCR is above or below 1.

S1 and S7 is not included in these observations as DNELs have not been derived for these substances. Due to lack of data it was not possible to derive DNELs for these substances within the scope of this project.

Looking at the formulation phase, the highest RCR(dermal) of approximately 7 is noted for S8 at uses 3 (activity related to the loading of solvent into mixing process), 12 (waste management) and 15, 16 (laboratory handling). A RCR of approximately 7 requires a PPE with an efficiency of approximately 90% in order to ensure safe use. An efficiency of 90% is expected to be obtained if the employee wears chemical-resistant gloves conforming to EN374 and has as a minimum of completed basic employee training and possibly also wears other appropriate dermal protection. For the use of NMP during the formulation phase RCRs of approximately 3 are reached for uses 3 (activity related to the loading of solvent into mixing process), 12 (waste management) and 15, 16 (laboratory handling), see Appendix 4.

Looking at the end-use phase, the highest RCR(dermal) of approximately 4-5 is noted for S8 at uses 31, 32, 33 (application of the paint). This requires a PPE with an efficiency of approximately 80% in order to ensure safe use. An efficiency of 80% is expected to be obtained if the employee wears chemical-resistant gloves conforming to EN374 and possibly also wears other appropriate dermal protection. For NMP RCR>1 is also reached for several uses in the end-use phase (B12, B13, B14, B15, B16, B17).

The mixtures M1, M2, M3, M4 appear to have RCRs below 1, so the dermal exposure to the mixtures are not expected to exhibit a risk to workers. RCRs(dermal) above 1 is noted for mixture M5 for the uses: 15, 16, 26-33. Uses are described in Appendix 4

4.2.1.3 Environmental exposure

Figure 6 compares the calculated RCR for surface water for the considered alternatives and mixtures. The considered alternatives are found to have environmental RCRs on the same level 0.01-0.08 – and all well below 1. Thus, the solvents use is of no risk to the aquatic environment in surface water.

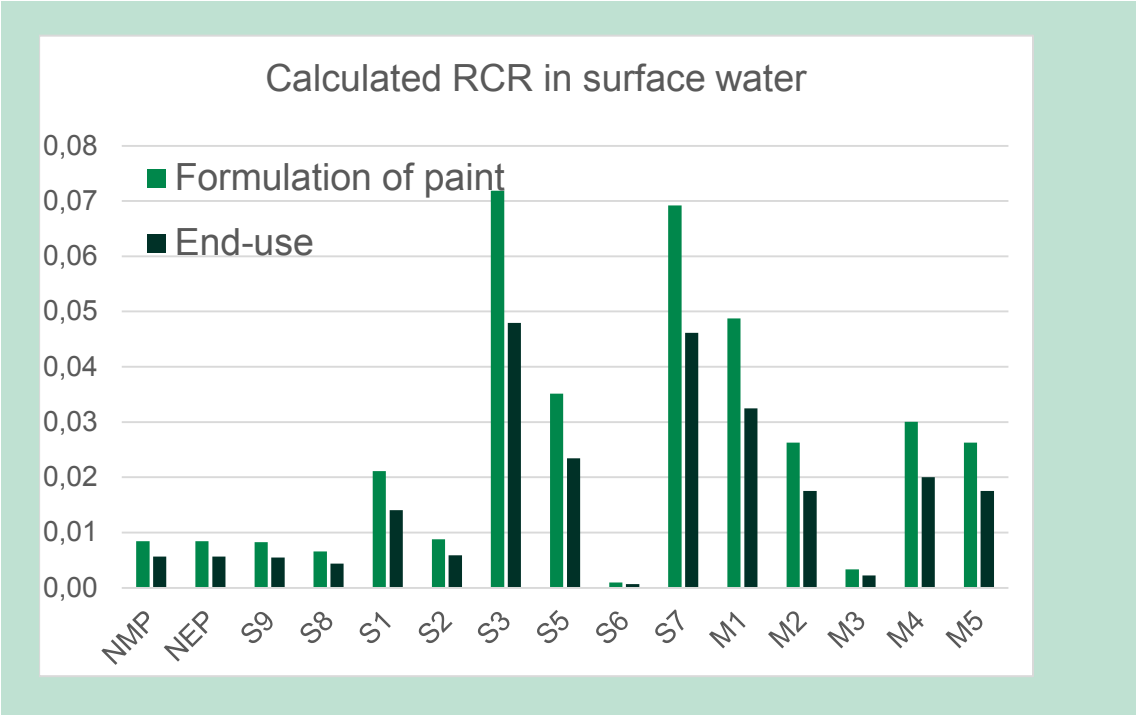

Figure 6. Comparison of RCRs for surface with for the considered substances and mixtures.

The highest observed RCRs are seen for the S3 and S7 and S5 and mixtures of S3 (M1, M4).

Looking at the RCR(environment) then the general sorting order is (compounds with the same color has the approximate same level of RCRs):

S3 > S7 > M1 > S5 > M4 > M5 > M2 > S1 >S2 > NMP > NEP >S9 > S8 > M3 > S6

Again, the red formatting color indicates the highest RCRs and the green color indicates the lowest RCRs, but the color does not indicate whether or not the corresponding RCR is above or below 1.

Thus, the apparently best option when considering the RCRs for environmental exposure appears to be S6 and the S3 appears to exhibit the highest risk to the environment. The PNEC for NMP, NEP and S8 was derived using relatively high assessment factors compared to the other substances. This partly explains their lower RCRs. It is also recalled that the assessment factor used for the derivation of PNEC for S8 and S6 was 1000, which together with their low RCRs indicate their low acute toxicity.

Overall, all alternatives appear to be safe with respect to the environment.

4.2.2 Conclusion

The RCRs for inhalation, dermal exposure and the environment do not follow a unique trend, so a conclusion on the best alternative cannot be made without making a prioritization of the relative importance of the inhalation and dermal exposure. In the order of RCRs for each exposure given below, only substances that have been performance tested in this project are included:

RCR(Inhalation): S3>S7>NEP>NMP>M4>M1>M5>S2>M2>M3>S6

RCR(Dermal): NEP>NMP>M5>S2>M1>M2>S3>M4>M3>S6

RCR(Environment): S3>S7>M1>M4>M5>M2>S1>S2>NMP>NEP>M3>S6

The red formatting color indicates the highest RCRs and the green color indicates the lowest RCRs. Solvents and mixtures with the same color have similar RCR values, but the color does not indicate whether or not the corresponding RCR is above or below 1.
From a human health perspective, S3 and S7 appear to be poor alternatives to NMP. For S7, this is only based on the calculated risk for exposure via inhalation since no DNEL for dermal exposure can be derived. However, a prioritization strategy with respect to human health should be – in agreement with the criteria for a substance to be placed on the candidate list - that the very severe CMR-properties of NMP overrules a prioritization with respect to high RCR-values.

The other substances and mixtures used for performance testing in paint all result in lower RCRs than NMP and NEP when considering human health.

All alternatives together with NEP and NMP appear to be safe with respect to the environment. The difference in RCRs are within one order of magnitude, and it appears not so relevant to consider the environmental aspects when optimizing the suggested alternatives.

All alternatives are, however, considered acceptable from a safety perspective, but some of the uses and alternatives would require the use of PPE. The same is true for the use of NMP. The exposure risk of NMP seems to be controlled for exposure via inhalation (RCR<1 for all uses) while risk is identified (RCR>1) for dermal exposure for both formulation work activities and use activities.

4.3 Characterization of the interface between PVC and coating using RAMAN spectroscopy

Raman spectroscopy is a strong tool for analyzing surfaces and interfaces as these can be mapped in relation to the precedence of specific substances. Such mappings can therefore show the presence of one compound in another compound matrix. Consequently, this can be used to characterize the penetration depths of specific substances into different materials. In another project partly funded by the Danish EPA, Raman spectroscopy was successfully used to analyze the penetration depth of paint into wood[19]. Raman spectroscopy was therefore tested as a method for enhancing the knowledge of the interface interaction between the PVC, and the paint formulated with and without solvent.

The penetration of the polymer coating into PVC is currently mostly characterized indirectly using e.g. adhesion tests. RAMAN analyses of the polymer-coating interface were performed to test if the paint adhesion enhancement by NMP, NEP and the substitution alternatives could be qualified and possibly quantified with this technique.

Two samples were chosen as test-objects for the evaluation of the analytical method, each assumed to represent a low and high degree of penetration into the material: the reference formulation without solvent and the reference formulation with NEP.

Results from the Raman analyses revealed the distribution of main components of the coating formulation (e.g. binder and pigment components) at the interface between coating and PVC. The Raman mapping of the interface revealed that using this method for analysis and data processing, the two materials (PVC and coating components) look sharply divided; i.e. the PVC did not show any clear signs of intermingling with the coating.

Different methods for data processing were applied to investigate if other means of quantification could be used to document any differences between the samples. Microscopic images were taken as well as RAMAN mapping of major components, which are shown in Figure 7 and **Fejl! Henvisningskilde ikke fundet.**Figure 8**Fejl! Henvisningskilde ikke fundet.Fejl! Henvisningskilde ikke fundet.Fejl! Henvisningskilde ikke fundet.**.

The microscopic images show the roughness of the interface between the coating and the PVC material. From the mapping, it is possible to identify major components such as the polymers used in the coating as well as the PVC. The depth profiles show the position of these components and how their intensity changes vertically down through the samples. The interface region is characterized by significant changes in the composition. As expected, the polymers from the coating have a high intensity at the top of the surface, but at approximately 40 µm depth, the interface between the coating and the PVC is reached and the signal from PVC begins to increase until the pure PVC region is reached and the PVC signal again becomes stabile.

By looking at the depth profiles on the right of Figure 7and Figure 8, it is possible to see the width of the transition from coating to PVC (the interface region marked by double horizontal lines), which seems to be approximately 4.3 µm for the sample without solvents and 7.5 µm for the sample with NEP. While the expanded interface of the paint containing adhesion promoting solvents provides a possible explanation for the enhanced performance observed in the selected AAMA tests (fx window cleaner test), the uncertainties of this particular analysis are currently determined by the step size of the measurements (1.2 µm) resulting in an uncertainty of approximately ±2 µm. Therefore, the differences in interfaces cannot be considered as

[19] MST-141-01416 (Fungicidfri grunder), not published

significant, and a larger data set is needed for statistical calculations and further development of the method.

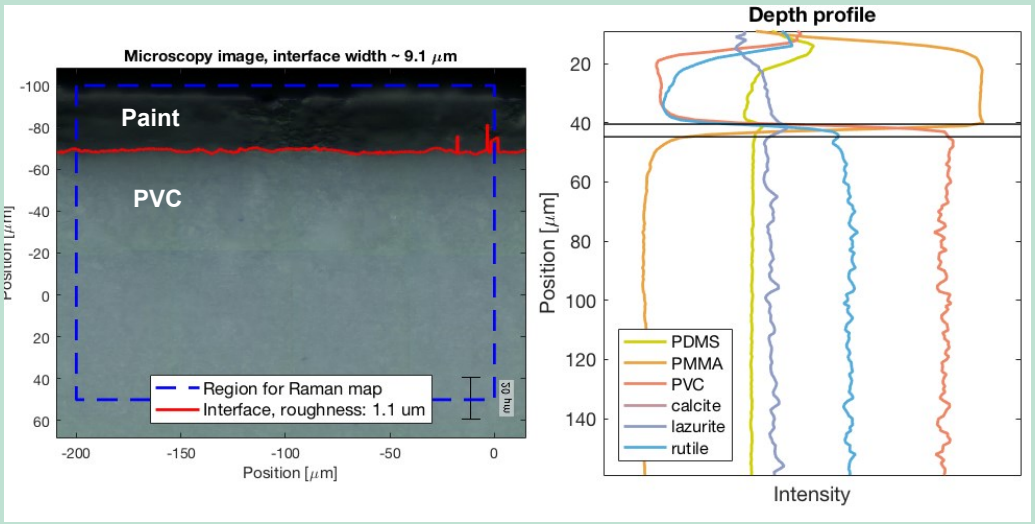

Figure 7. Microscopic imaging (left) and Raman mapping analysis of the reference sample without solvents, depth profile (right) with the interface region marked by two horizontal lines.

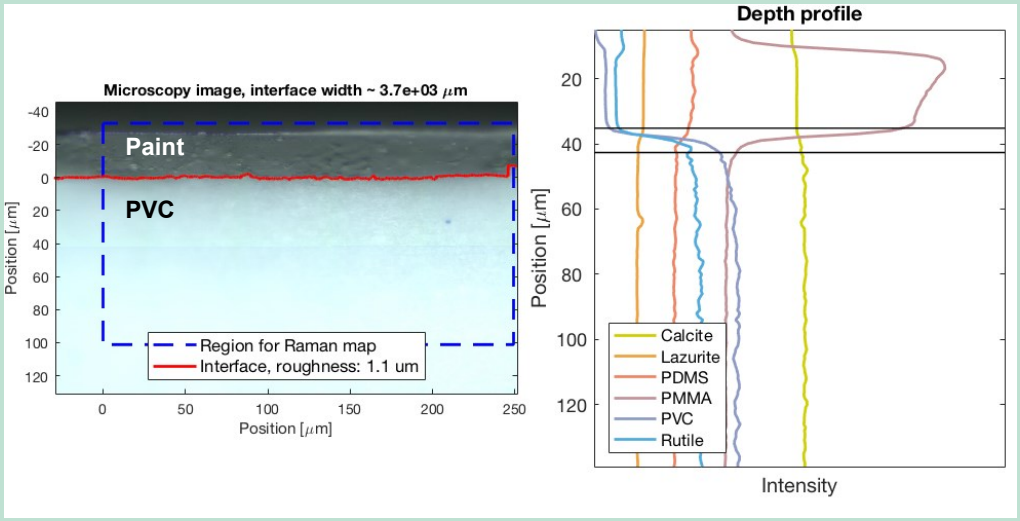

Figure 8. Microscopic imaging (left) and Raman mapping analysis of the reference sample with NEP, depth profile (right) with the interface region marked by two horizontal lines.

Neither of the used methods for data processing provided clear differentiation between the samples. However, initial results indicated that sample preparation and measuring parameters had a great impact on the outcome of the data processing.

At similar measuring parameter settings and sample preparation, data indicated that a combination of randomly located RAMAN mapping of the interface between coating and PVC and optical spectroscopy, combined with advanced image processing algorithms, could prove to be a future method for analyzing interfaces of this type. However, the development of such a method was considered to be outside the core topic and timeframe of this project. Also, there is no guaranty that this type of characterization of the interface can be directly related to adhesion properties.

4.3.1 Conclusion

From the results, it was concluded that at the current stage, the RAMAN analytical method is not capable of clearly differentiating between samples with and without the known penetration enhancer NEP in terms of penetration of the coating into the PVC. It can therefore not be used to study the penetration depth of the selected alternative solvents and thereby increase the understanding of their adhesion enhancing properties.

5. Overall conclusion

It is estimated that by 2020 more than 3-4 million PVC windows will be produced[20]. The NMP containing paint needed for these PVC windows correspond to a global potential for substitution of NMP of 600 tonnes. The aim of this project was to identify alternative solvents, capable of replacing NMP and NEP in paint for PVC.

Possible alternative solvents were identified using the Hansens Solubility Parameters in Practice software, where identification of solvent alternatives based on structural similarity to NMP and NEP was avoided, in order to maximize the possibility of finding an alternative with a less hazardous profile. All solvents were initially screened for price and health and environmental properties, and acceptable candidates were then formulated directly in a paint system and subsequently subjected to a selection of performance tests. The selected candidates were also evaluated thoroughly in relation to the health and environmental impact of these compounds. Based on the test results and the health and environmental evaluation, compounds were in- or excluded from being taken further in the process of making a non-NEP and -NMP containing paint product for PVC.

Of the 21 initially identified solvents a total of three solvents (S2, S3 and S7) were found applicable as possible alternatives, capable of substituting NMP and NEP in PVC paint. These alternatives showed excellent performance regarding formulation compatibility and stability, wet and dry adhesion as well as visual appearance after cold crack testing. Also these three solvents are commercially available through known or identified suppliers. The solvent S1 passed all tests, but exhibited some undesired changes in visual appearances. Also, this substance could not be assessed regarding dermal exposure and exposure through inhalation due to lack of a derived DNELs. S6 exhibited good performance in the window cleaner test and only had some visually appearance changes during the cold crack test, though results from adhesion tests are currently not available for S6.

Summing up; solvents S2, S3 and S7 exhibited excellent performance in the selected tests, indistinguishable, from the performance of NEP and NMP. However, S3 and S7 appear to exhibit a higher risk to workers – but the risk can be controlled using proper personal protection equipment. It is not possible to evaluate the risk of dermal exposure for S7 since no NDEL is available due to lack data. For NMP the exposure risk seems to be controlled for exposure via inhalation (RCR<1 for all uses) while risk is identified (RCR>1) for dermal exposure for both formulation work activities and use activities. A prioritization strategy with respect to human health should be – in agreement with the criteria for a substance to be placed on the candidate list - that the very severe CMR-properties of NMP overrules a prioritization with respect to high RCR-values.

S2 is clearly a better alternative to NEP and NMP showing lower RCRs both with respect to inhalation and to dermal exposure. However, S2 is currently only sourced through one known supplier and at a higher price than NMP and hence do not meet the criteria set for price at the initiation of the project. For S3 and S7 the availability is considered more stable and the price is lower than for S2, although still higher than the price of NMP.

[20] http://www.ceresana.com/en/market-studies/industry/windows-and-doors-europe/

All alternatives together with NEP and NMP appear to be safe with respect to the environment. The difference in RCRs for the environment are within one order of magnitude, and it does not appear relevant to consider the environmental aspects when choosing the best alternative.

To identify even more potential alternatives for NMP than the singe substances represent, mixtures, also proposed by HSPiP, were tested for their respective performance. Of the mixtures, only M4 passed the window cleaner test, whereas all the other mixtures exhibited blisters during the test. The best performing mixture did however, contain a compound, which are evaluated to be not readily degradable, thus this mixture did not continue for further formulation. It also contains a substance that even at low dermal exposure levels is absorbed through the skin, which is unpleasant for the user and hence unacceptable.

All tested single solvents or solvent mixtures perform acceptable when testing dry and wet adhesion. However, the negative reference sample without solvent also pass the adhesion test.

In addition to finding NMP substitution candidates, this project has shown the strengths and applicability of HSPiP as a tool for identifying solvents and solvent mixtures for substituting problematic solvents. By using HSPiP, solvents were quickly identified for practical tests based on the theoretical calculations performed by the software. The HSPiP tool speeds up the substitution process and reduces the work effort involved in a typical trial-and-error based approach.

In order to implement the NMP substitutes in the production at Teknos and preparing an NMP-free product for the marked, Teknos is currently working on documenting the long-term performance of the final product and ensuring that the paint containing the alternatives identified in this project actually complies with requirement set by Teknos and their customer. This will be done by subjecting formulations containing selected single solvents or mixtures to additional performance tests, including an accelerated weathering test over a longer period of time.

Appendix 1.
List of Abbreviations

Abbreviation	Explanation
CEPE	European Council of the Paint, Printing Ink and Artists' Colours Industry
CLP	Classification, Labelling and Packaging of chemicals
CMR	Carcinogenic Mutagenic (toxic to) Reproduction
CoRAP	Community rolling action plan
DG	Dangerous Goods
DNEL	Derived No Effect Level
ECETOC TRA	Targeted Risk Assessment tool from European Centre For Ecotoxicology and toxicology of Chemicals
EC50	Concentration at which 50% of the test species are affected
ED	Endocrine Disruptor
Env. Class.	Environmental Classification
EUSES	The European Union System for the Evaluation of Substances
LC50	Concentration at which 50% of the species dies during the test
PBT	Persistent Bioaccumulative Toxic
PEC	Predicted Environmental Concentration
PG	Packaging Group
PNEC	Predicted No Effect Concentration
QSAR	Quantitative Structure Activity Relationship
RCR	Risk Characterisation Ration
SVHC	Substance of Very High Concern
VOC	Volatile Organic Carbon
vPvB	Very Persistent Very Bioaccumulative

Appendix 2. Alternative methods and pre-treatment

Modification of the surface of PVC

A literature screening was performed to obtain knowledge of possible solutions for phasing out the use of NMP that does not involve replacing the solvent in the actual paint formulation. The following contains an overview of alternative methods and treatments intended for this[21].

Appendix 2.1 Sandpaper

When using sandpaper to modify the PVC surface, mechanical force is applied. As the surface is scratched, physical pores form in the surface. Sandpaper is cheap and easily accessible, but treated surfaces appear uneven causing an inhomogeneous color.

Appendix 2.2 Sandblasting

With this type of treatment, the surface will be shelled with sand. This will, similar to sandpaper, form pores in the surface, so the paint can easier attach to the surface when applied. It is easy and inexpensive. However, the same problems arise as when using sandpapering. The sandblasting constitutes an extra production step for the user before applying the paint provided by Teknos, thus introducing the risk of making the non-NMP Teknos product less competitive.

Appendix 2.3 UV light

It is a known fact that when untreated PVC breaks down when exposed to light.[22]
Using UV light as a source to create pores in the PVC will increase the adhesion.[23]
Today, UV-light treatment is used in the industry, but some customers may not have the equipment in-house, and the addition of an extra production step before applying the paint introduces the risk of making the non-NMP Teknos product less competitive.

Appendix 2.4 Plasma treatment

Plasma treatment is used to modify a plastic surface by bombarding the surface with ionized gas. The gas selected for plasma treatment can vary; some of the commonly used gases are argon, helium, nitrogen, and oxygen. This treatment results in the introduction of amine, carboxyl, hydroxyl, and aldehyde groups on the surface of the plastic. These functional groups increase the surface activation and surface energy of the plastic. The increase in surface energy leads to a comparable increase in adhesive wet out and consequently adhesive strength.[24] [25] However, some customers may not have the equipment in-house, and the addi-

[21] Surface modification of PVC films in solvent–non-solvent mixtures J. Sacrista´n, H. Reinecke*, C. Mijangos
[22] http://www.sciencedirect.com/science/article/pii/S1658365514000880#sec0055
[23] https://www.ellsworth.com/globalassets/literature-library/manufacturer/henkel-loctite/henkel-loctite-design-guide-plastic-bonding.pdf
[24] http://na.henkel-adhesives.com/us/content_data/389654_effect_of_surface_treatment_on_difficult_to_bond_plastics_92315.pdf
[25] http://sabreen.com/surface_wetting_pretreatment_methods.pdf

tion of an extra production step before applying the paint introduces the risk of making the non-NMP Teknos product less competitive.

Appendix 2.5 Heat treatment

Heat treatment increases the adhesion to plastics by exposing the plastic to a blast of hot air (approximately 500°C) or an open flame, known as thermal and flame treatment respectively. These techniques oxidize the surface introducing functionality such as hydroxyl, carbonyl, carboxyl, and amide groups to the surface (typical oxidation depth of approximately 4 to 9 nanometers). The introduction of polar groups results in increased adhesion. Some hydroperoxide groups are also formed. Thermal treatment may also utilize a free radical mechanism accompanied by chain scission and some crosslinking. However, some customers may not have the equipment in-house, and the addition of an extra production step before applying the paint introduces the risk of making the non-NMP Teknos product less competitive.

Appendix 2.6 Chemical modification of the PVC surface using solvents

Prior to the application of the paint coating, a suitable solvent capable of dissolving the surface of PVC can be applied as a pretreatment. Dissolution of the surface results in pore formation (comparable to the effect of NMP in the paint), penetration, softening and eventually dissolution of the PVC material, consequently damaging the PVC surface if exposure time is not appropriately controlled.[26] Examples of solvents used are DMSO and Acetone (or alternatives with similar properties and a better health and environmental profile). The low rate of evaporation of DMSO can cause the surface modification to be uneven, resulting in color differences when the final coating is applied. Acetone evaporates faster, although an alternative with less harmful effects would be preferable. Other possible solvents might be identified using a PVC resistant chart.[27] An alternative solvent might be identified from a list produced using the HSPiP software.

Teknos could produce the surface pretreatment product for their customers in addition to the paint.

A disadvantage for the customers is the addition of an extra production step, as they must treat the surface before applying the paint.

Appendix 2.7 Additives in the paint

Surface tension of the paint can be reduced by the addition of additives. The surface tension of the paint should be lower than the surface tension of PVC, which is 41 dynes.

Surface tension of the paint can be reduced by adding low surface tension chemicals, such as hydrocarbon or polymethyl siloxane solutions (PDMS). For example, hydrocarbon xylene has a surface tension of 29 dynes.

Other low tensile additives could be MEK (25 dynes), Butyl glycol (27 dynes), Mineral spirits (25-35 dynes).[28]

However, some surface tension additives carry unacceptable hazard classifications, e.g. xylene[29], butyl glycol[30]

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[26] http://depts.washington.edu/open3dp/2015/01/polymer-guide-if-you-seek-solvation/

[27] http://www.goodyearrubberproducts.com/files/PacEchoSunflow/PacEchoSunflow/PacEchoSunflow1.Page43.pdf

[28] http://www.pcimag.com/articles/101826-solving-film-defects-with-surface-tension-modifiers

[29] https://echa.europa.eu/da/substance-information/-/substanceinfo/100.014.124?_disssubsinfo_WAR_disssubsinfoportlet_backURL=https%3A%2F%2Fecha.europa.eu%2Fda%2Fsearch-for-chemicals%3Fp_p_id%3Ddisssimplesearch_WAR_disssearchportlet%26p_p_lifecycle%3D0%26p_p_state%3Dnormal%26p_p_mode%3Dview%26p_p_col_id%3Dcolumn-1%26p_p_col_count%3D1%26_disssimplesearch_WAR_disssearchportlet_sessionCriteriaId%3DdissSimpleSearchSessionParam101401505309574968

and MEK[31].

Appendix 2.8 Addition of surfactants

The addition of surfactants reduces the surface tension of water-based paint to make it lower than the PVC surface. This reduces the contact angle between the paint and the PVC surface and allows the paint to "wet" the PVC surface better. The smaller the contact angle, the better the interactions between the paint and the PVC surface.
Surfactants that reduce surface tension can be nonionic, anionic and cationic.
Fluorosurfactants, silicone surfactants and other organic surfactants are good at wetting the PVC surface. This will provide a better attachment to the surface. [32]
Some other companies already use silicone as surfactants.[33] The Danish EPA has previously made an overview of surfactants in use at different companies.[34]
The disadvantage is that the surfactants diffuse up to the surface of the paint and evaporate before the paint is dry, causing defects in the coloration.[35] Depending on the choice of surfactant this might also affect the paint formulation. It is thus necessary to investigate the optimal choice of surfactants for each formulation and application.

Appendix 2.9 Corona treatment

In a corona discharge process, the plastic is exposed to an electrical discharge, usually in the presence of air and at atmospheric pressure in order to create a plasma field. This roughens the surface, which provides sites for mechanical interlocking, and introduces reactive sites on the plastic's surface, consequently increasing the wettability and reactivity of the surface. The reactive functionalities, which are theorized to be introduced to the surface may include, but are not proven to be, carbonyl, hydroxyl, hydro peroxide, aldehyde, ether, ester, and carboxylic acid groups, as well as unsaturated bonds.[36] However, some customers may not have the equipment in-house, and the addition of an extra production step before applying the paint introduces the risk of making the non-NMP Teknos product less competitive.

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[30] https://echa.europa.eu/da/substance-information/-/substanceinfo/100.003.550

[31] https://echa.europa.eu/da/substance-information/-/substanceinfo/100.014.124?_disssubsinfo_WAR_disssubsinfoportlet_backURL=https%3A%2F%2Fecha.

[32] http://www.afcona.com.my/Slip_and_Leveling_agent_mar_2010.pdf
http://www.pcimag.com/ext/resources/VirtualBrochure/Air_Products_Dynol.pdf

[33] http://www.firp.ula.ve/archivos/material_web_4xx/04_CESIO_Scholz_187.pdf

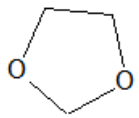
[34] http://www2.mst.dk/common/Udgivramme/Frame.asp?http://www2.mst.dk/udgiv/publications/2005/87-7614-668-5/html/kap05_eng.htm

[35] http://www2.benjaminmoore.com/en-us/for-your-home/surfactant-leaching

[36] https://www.ellsworth.com/globalassets/literature-library/manufacturer/henkel-loctite/henkel-loctite-design-guide-plastic-bonding.pdf

Appendix 3. Screening of alternative substances

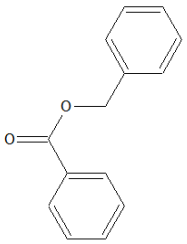
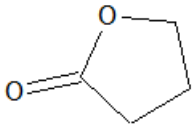
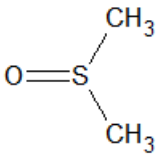
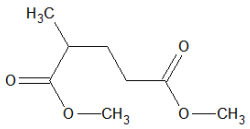
Appendix 3.1 Screening of alternatives, where no conclusions regarding SVHC – properties could be made on the basis of the initial REACH screening

1,3 – dioxalane (646-06-0)

SVHC-properties
PBT: Not acceptable
Not readily biodegradable (1) =>may be a P-substance logKow: -0.37 (7)=>is not a B-substance The lowest acute toxicity was LC50(fish, 96hr)>95.4 mg/L=>not a T-substance **Not PBT**
Not vPvB (see above)
The harmonized classification does not include any CMR-classification phrases. The substance is on CoRAP list as suspected for toxicity to reproduction and mutagenic toxicity Data in VEGA (4) shows no mutagenic properties. Some indications of mutagenic properties (3) Read-across to 1,4 dioxane (which is classified as carcinogenic) may indicate carcinogenic properties. **It cannot be excluded that the substance may have CMR-properties. Therefore, it is recommended not to include this substance at the moment. Any considerations of including the substance should await the conclusions from CoRAP.**
Not on list* (3)/(4): Estrogen Receptor Binding: No affinity/Not active (Possible non-active) **No indication of endocrine disruptor properties**
Not classified for environmental hazard
Not classified with respect to Acute Tox **=>No acute toxicity**

1,3 – dioxalane (646-06-0)
BP: 78°C **=>the substance is as a VOC, as the boiling point is below 250°C**
No data
UN ADR/RID:1166, ADR/RID: 3; IDMG 3, IATA 3; Packaging group II Concentration limit:

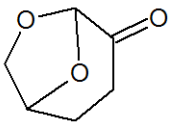
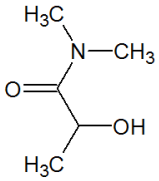
*http://ec.europa.eu/environment/chemicals/endocrine/pdf/final_report_2007.pdf

Appendix 3.2 Screening of selected alternatives

benzyl benzoate (120-51-4)	gamma-butyrolactone (96-48-0)	DMSO (67-68-5)	Dimethyl 2-methylgluterate (19013-37-7)
			
SVHC-properties			
PBT: Not acceptable			
Readily biodegradable (1)=>not P $LogK_{OW}$: 3.97 (1) => has some potential of bioaccumulation Lowest acute toxicity E(L)C50: 0.29 mg/L (fish, 96 hr); lowest chronic toxicity NOEC/EC10: 0.25-0.26 mg/L (algae and daphnia) (1)=>not T **Not PBT**	Readily biodegradable (1)=> not P $logK_{OW}$: -0.57 (1) =>not B Lowest acute toxicity E(L)C50: 56 mg/L (fish, 96 hr); lowest chronic toxicity EC10: 84 mg/L (algae) (1)=>not T **=>not PBT**	Not readily biodegradable (1) =>may be a P-substance logKow: -1.35 (1)=>is not a B-substance The acute toxicity to fish, crustacean and algae are >>100 mg/L (1)=>not a T-substance **Not PBT**	Readily biodegradable (2) Readily biodegradable (read-across to Dimethyl glutarate (1119-40-0)) =>is not a P-substance logKow: 1.31 (2)=>is not a B-substance lowest acute toxicity (fish): 30.9 ppm (V/V) (read-across to Dimethyl glutarate (1119-40-0)) =>not T **Not PBT**
SVHC-properties			
vPvB: Not acceptable			
Not vPvB (see above)	**Not vPvB** (see above)	**Not vPvB** (see above)	**Not vPvB** (see above)
SVHC-properties			
CMR: Carc. 1A;Carc. 1B; Muta. 1A; Muta. 1B; Repr. 1A; Repr. 1B Not acceptable			
The substance is not a CMR-substance (1, 8) The substance is not C,M (exp. data in ref. 4)	Not C (1); not M (1); R: Inconclusive but data does not indicate significant toxicity to reproduction (1) VEGA predictions indica-	The substance is not classification for human health hazard. However, data on carcinogenicity are lacking (1) No/low indication of car-	The read-across substance (Dimethyl glutarate (1119-40-0)) is not classified human health hazard. However, data on Carcinogenic and toxicity to

benzyl benzoate (120-51-4)	gamma-butyrolactone (96-48-0)	DMSO (67-68-5)	Dimethyl 2-methylgluterate (19013-37-7)
=>No indication of CMR-properties	tion not R, but the reliability is low. **=>No indication of CMR-properties**	cinogenicity (3)(4) The substance has not been identified as likely, possible or confirmed carcinogen to humans of the IARC **=>No strong indication of CMR properties**	reproduction are lacking. With reference to the substances (from ECHA CLP Inventory), which are classified as being toxic to reproduction, there is no structural alerts of Dimethyl 2-methylgluterate indicating toxicity to reproduction. No/low indication of carcinogenicity (3) Some indication of carcinogenicity (low-moderate reliability) (4) **=>No strong indication of CMR properties**
SVHC-properties			
Endocrine disruptor: Known endocrine disruptor (ED) Or Strong indications of endocrine disruptor properties Not acceptable			
Not on list* There is no indication of ED-properties within the model domains in (3, 4). **No indication of endocrine disruptor properties**	Not on list* There is not indication of ED-properties within the model domains in (3,4) **No indication of endocrine disruptor properties**	Not on list* (3)/(4): Estrogen Receptor Binding: No affinity/Not active (Possible non-active) **No indication of endocrine disruptor properties**	Not on list* (3)/(4): Estrogen Receptor Binding: No affinity/Not active (Possible non-active) **No indication of endocrine disruptor properties**
Classification			
Env. Class.: Aquatic Acute 1 (H400); Aquatic Chronic 1 (H410); Aquatic Chronic 2 (H411): Not preferred			
The substance has a harmonized classification of: Acute Tox. 4* H302 Aquatic Chronic 2 H411 Concentration limit:	**Not classified for environmental hazard**	**Not classified for environmental hazard**	**Not classified for environmental hazard**
Classification			
Acute Tox.: Acute Tox. 1, Acute Tox. 2, Acute Tox. 3: Not acceptable. Maybe acceptable on substance level			
Not classified for acute toxicity (sufficient data are available) **=>No acute toxicity**	Not classified with Acute Tox. 1, Acute Tox. 2, Acute Tox. 3 **=>Not classified with Acute Tox1, Tox2 Tox3**	Not classified with respect to Acute Tox **=>No acute toxicity**	The read-across substance (Dimethyl glutarate (1119-40-0)) is not classified with respect to Acute Tox **=>No acute toxicity**
Other			

benzyl benzoate (120-51-4)	gamma-butyrolactone (96-48-0)	DMSO (67-68-5)	Dimethyl 2-methylgluterate (19013-37-7)
VOC (BP <250°C): Not preferred			
BP: >250 °C (1) **=> not VOC**	BP: 204°C **=>the substance is as a VOC, as the boiling point is below 250°C**	BP: 189°C (decomposes at 190°C) (1) **=>the substance is as a VOC, as the boiling point is below 250°C**	BP: 174°C (2) **=>the substance is as a VOC, as the boiling point is below 250°C**
Other			
Odor: Not preferred			
No data	No data	No data	No data
Other			
Dangerous Goods (Classification under transport regulation): Not preferred			
UN (ADR, IDMG, IATA): 3082 ADR, IDMG, IATA 9 Packaging group III Concentration limit:	ADR/RID/IDMG/IATA/ICAO: Not dangerous goods (9)	ADR/RID/IMDG/IATA: Not dangerous goods (9a)	ADR/RID/IMDG/IATA: Not dangerous goods (9a)

Cyrene 53716-82-8	Loxanol MI 6470 35123-06-9	Dibasic esters (1119-40-0/106-65-0/627-93-0)
		Dimethyl glutarate (DG) (1119-40-0) Dimethyl succinate (DS) (106-65-0) Dimethyl adipate (DA) (627-93-0)
SVHC-properties		
PBT: Not acceptable		
Readily biodegradable (1) =>not P logKow: 0.021 (1) => not B lowest acute toxicity E(L)C50 >100 mg/L (1); EC10(algae, 72hr)>100 mg/L =>not T	Readily biodegradable (1) =>not P logKow: -0.94 (1) =>not B The lowest acute toxicity E(L)C50 >100 mg/L (1); the lowest chronic toxicity (for Daphnia magna)>=12 mg/L (1) =>not T	All three substances are readily biodegradable (1) =>not P $logK_{OW}$ (DG): 0.49 (1) $logK_{OW}$ (DS): 0.33 (1) $logK_{OW}$ (DA): 1.4 (1) =>not B Lowest acute toxicity E(L)C50: DG:>32 mg/L (1) DS: >50 mg/L (1) DA: >18 mg/L (1) Lowest chronic toxicity

Cyrene 53716-82-8	Loxanol MI 6470 35123-06-9	Dibasic esters (1119-40-0/106-65-0/627-93-0)
Not PBT	**Not PBT**	EC10/NOEC DG:36 mg/L DS:>100 mg/L DA:12.4 mg/L **=>not PBT**
SVHC-properties		
vPvB: Not acceptable		
Not vPvB (see above)	**Not vPvB** (see above)	**Not vPvB** (see above)
SVHC-properties		
CMR: Carc. 1A;Carc. 1B; Muta. 1A; Muta. 1B; Repr. 1A; Repr. 1B Not acceptable		
CMR: no data (1) IARC: The substance is not identified as likely, possible or confirmed carcinogenic to human subjects by the IARC (5). Non-carcinogen (CAESAR, ISS); Carcinogen (IRFMN/Antares) (low reliability (4) **=>No positive indication of C-properties** Bacterial mutagenicity reverse test, Salmonella typhimurium. Results: negative (5) Cyrene demonstrated no mutagenicity (OECD No. 471 and 487) (7) **=>No positive indication of M-properties** The substance does not have any of the groups, which has been identified to substances with a harmonized classification with Repr 1A or Repr 1B[37]. **=>No positive indication of R-properties**,	C: no data (1) M: not mutagenic (1) R: negative (fertility, development) (1), no data (breastfed babies) Carcinogenicity: CASE Ultra+Leadscope: Negative **=>No indication of CMR-properties**	DG: not M (1). No data for carcinogenicity and toxicity to reproduction in the dossier. However, the CoRAP concludes that DG is not carcinogenic nor toxic to reproduction. DS: not classified for CMR (full data set) (1) DA: not classified for CMR (full data set) (1) **=>No indication of CMR-properties**
SVHC-properties		
Endocrine disruptor: Known endocrine disruptor (ED) Or Strong indications of endocrine disruptor properties Not acceptable		
Not on list* (3)/(4): Estrogen Receptor Binding: No affinity/Not active (Possible non-active) **No indication of endocrine disruptor properties**	Not on list* (3)/(4): Estrogen Receptor Binding: No affinity/Not active (Possible non-active) Androgen Receptor Antagonism (Human in vitro): negative (3) Pregnane X Receptor (PXR) Binding (human in vitro): negative **No indication of endocrine disruptor properties**	Not on list* DG was on the CoRAP due to suspected ED properties. However, the final CoRAP report concludes that the substance has no endocrine disruptor properties. **No indication of endocrine disruptor properties**

[37]Imides, Amides, Phenols, poly, Esters, Polynitrophenols, Thioureas , Substituted Ureas, Phenols, Imides, Ketone alcohols, Phenols

Cyrene 53716-82-8	Loxanol MI 6470 35123-06-9	Dibasic esters (1119-40-0/106-65-0/627-93-0)
Classification		
Env. Class.: Aquatic Acute 1 (H400); Aquatic Chronic 1 (H410); Aquatic Chronic 2 (H411): Not preferred		
Not classified for environmental hazard	**Not classified for environmental hazard**	**None of the three substances are classified for environmental hazard**
Classification		
Acute Tox.: Acute Tox. 1, Acute Tox. 2, Acute Tox. 3: Not acceptable. Maybe acceptable on substance level		
Acute toxicity oral: not classified (sufficient data are available) Acute toxicity dermal and inhalation: No data. The substance is readily taken up dermally (2) =>No clear conclusion, as only data on oral toxicity is measured. This indicates that the **substance is not acutely toxic.**	Not classified for acute toxicity (sufficient data are available) **=>No acute toxicity**	Not classified with respect to Acute Tox **=>No acute toxicity**
Other		
VOC (BP <250°C): Not preferred		
BP: 227°C (1) VP: 28 Pa (25°C) (1) **=>the substance may be characterized as a VOC, as the boiling point appears to be below 250°C**	BP: >224°C (1) BP: 217°C (2) VP: <12Pa (20°C) (1) VP: 3 Pa (25°C) (2) **=>the substance may be characterized as a VOC, as the boiling point (BP) appears to be below 250°C**	BP DG: 216°C(1) DS: 196°C (1) DA: 231°C (1) **=>the substance is as a VOC, as the boiling point is below 250°C**
Other		
Odor: Not preferred		
No data	No data	No data
Other		
Dangerous Goods (Classification under transport regulation): Not preferred		
ADR/RID: Not dangerous goods IMDG: Not dangerous goods IATA: Not dangerous goods (5)	ADR/RID: Not dangerous goods IMDG: Not dangerous goods IATA/ICAO: Not dangerous goods (5)	ADR/RID: Not dangerous goods IMDG: Not dangerous goods IATA/ICAO: Not dangerous goods (9)

Data references

(1): REACH registration dossier
(2): EpiSuite calculations
(3): MST QSAR
(4): VEGA
(5): SDS from Sigma-Aldrich

(6): SDS from BASF

(7): Jinfeng Zhang, Gabrielle B. White, Michaela D. Ryan, Andrew J. Hunt, and Michael J. Katz (2016): Dihydrolevoglucosenone (Cyrene) As a Green Alternative to N,N‑Dimethylformamide (DMF) in MOF Synthesis. ACS Sustainable Chemistry & Engineering 4(12),· September 2016

(7): EpiSuite (experimental data)

(8): ECHA list of notified CLP classifications

(9) SDS from Holmberg (http://www.holmberg.se/upload/product/files/msds-gamma-butyrolactone-gbl-eng-2011-10-07---641.pdf)

(9a): SDS from Sigma-Aldrich

Appendix 4.

Appendix 4.1 Uses and activities – formulation of paint (manufacturing)

#No	Activity	PROC	Duration Frequency	Outdoor	Activity no in this report
A1	*Receipt and storage of raw materials* - raw material delivery - packaged - solids and liquids - outdoor	PROC 3	4 - 8 hours 225 days per annum	Yes	1
A2	*Receipt and storage of raw materials* - raw material storage - indoor	PROC 3	4 - 8 hours 225 days per annum	No	2
A3	*Raw material assembly and charging* - raw material dispensing manually from bulk storage or packaged goods Liquids -indoor	PROC 8b	4 - 8 hours 225 days per annum	No	3
A4	*Blending/dissolving/ dispersion* - mixing, milling, dispersing, completion - batch - open - sampling	PROC 5	4 - 8 hours 225 days per annum	No	4
A5	*Blending/dissolving/ dispersion* - mixing, milling, dispersing, completion - batch - open - additions	PROC 5	4 - 8 hours 225 days per annum	No	5
A6	*Filtering and filling* -filtering or sieving and filling -dedicated lines - open	PROC 9	4 - 8 hours 225 days per annum	No	6
A7	*Manufacturing equipment cleaning* - open - in workplace - in-situ	PROC 5	4 - 8 hours 225 days per annum	No	7
A8	*Manufacturing equipment cleaning* - open - in workplace - off-line	PROC 5	4 - 8 hours 225 days per annum	No	8
A9	*Waste management* - transfer of process wastes to storage containers - in workplace - off-line	PROC 8b	4 - 8 hours 225 days per annum	No	9
A10	*Waste management* - storage of waste prior to removal for off-site management	PROC 3	4 - 8 hours 225 days per annum	Yes	10
A11	*Waste management* - solvent recovery - condensation or adsorption/ desorption processes	PROC 3	4 - 8 hours 225 days per annum	Yes	11
A12	*Waste management* - transfer of recovered solvent into bulk storage tanks or IBCs	PROC 8b	4 - 8 hours 225 days per annum	Yes	12
A13	*Manufacturing equipment maintenance* - opening of manufacturing equipment and pipework containing chemicals for repair	PROC 8b	4 - 8 hours 225 days per annum	No	13
A14	*Manufacturing equipment maintenance* - cleaning manufacturing equipment for maintenance purposes	PROC 8b	4 - 8 hours 225 days per annum	No	14
A15	*Laboratory use* - QC laboratory	PROC 5	4 - 8 hours 225 days per annum	No	15
A16	*Laboratory use* - R&D laboratory	PROC 5	4 - 8 hours 225 days per annum	No	16

Appendix 4.2 Uses and activities – industrial end use of paint

#No	Activity	PROC	Duration Frequency	Outdoor	Activity no in this report
B1	*product delivery/storage* - product delivery - packaged - outdoor	PROC 3	4 - 8 hours 225 days per annum	Yes	17
B2	*product delivery/storage* - product storage - indoor	PROC 3	4 - 8 hours 225 days per annum	No	18
B3	*product delivery/storage* - product storage - outdoor	PROC 3	4 - 8 hours 225 days per annum	Yes	19
B4	*preparation of material for application* - enclosed - liquid products	PROC 1	4 - 8 hours 225 days per annum	No	20
B5	*preparation of material for application* - continuous - closed - liquid products	PROC 2	4 - 8 hours 225 days per annum	No	21
B6	*preparation of material for application* - batch - indoor - liquid products	PROC 5	4 - 8 hours 225 days per annum	No	22
B7	*preparation of material for application* - transfer of material from one container to another - liquid coatings	PROC8b	4 - 8 hours 225 days per annum	No	23
B8	*loading of application equipment* - enclosed - liquid coatings	PROC 1	4 - 8 hours 225 days per annum	No	24
B9	*loading of application equipment* - continuous - closed - liquid products	PROC 2	4 - 8 hours 225 days per annum	No	25
B10	*loading of application equipment* - batch - indoor - liquid products	PROC8b	4 - 8 hours 225 days per annum	No	26
B11	*loading of application equipment* - transfer of material from one container to another - liquid products	PROC8b	4 - 8 hours 225 days per annum	No	27
B12	*Application* - on-line - roller, spreader, flow coating *or* printing - open equipment - large scale - liquid coatings - printing inks	PROC 10	4 - 8 hours 225 days per annum	No	28
B13	*Application* - on-line - roller, spreader, flow coating *or* printing - enclosed equipment - large scale - liquid coatings - printing inks [e.g. publication gravure]	PROC 10	4 - 8 hours 225 days per annum	No	29
B14	*Application* - on-line - roller, spreader, flow coating *or* printing - open equipment - small scale - liquid coatings - printing inks	PROC 10	4 - 8 hours 225 days per annum	No	30
B15	*Application* - on-line - automatic/robotic spray coating *or* printing enclosed equipment - liquid coatings - printing inks	PROC 7	4 - 8 hours 225 days per annum	No	31
B16	*Application* - on-line - manual spraying - open equipment - liquid coatings	PROC 7	4 - 8 hours 225 days per annum	No	32

#No	Activity	PROC	Duration Frequency	Outdoor	Activity no in this report
B17	*Application* - off-line - manual spraying - open equipment - liquid products	PROC 7	4 - 8 hours 225 days per annum	No	33
B18	*film formation* - airdrying	PROC 4	4 - 8 hours 225 days per annum	No	34
B19	*film formation* - force drying (50 - 100C)	PROC 2	4 - 8 hours 225 days per annum	No	35
B20	*Application equipment cleaning* - enclosed - indoor - off-line	PROC 3	4 - 8 hours 225 days per annum	No	36
B21	*Application equipment cleaning* - open - indoor - in-situ	PROC 5	4 - 8 hours 225 days per annum	No	37
B22	*Application equipment cleaning* - open - indoor - off-line	PROC 5	4 - 8 hours 225 days per annum	No	38
B23	*laboratory use* - QC laboratory	PROC 5	4 - 8 hours 225 days per annum	No	39
B24	*waste management* - storage of waste prior to removal for off-site management	PROC 3	4 - 8 hours 225 days per annum	Yes	40
B25	*waste management* - transfer of process wastes to storage containers - in workplace - off-line	PROC 8b	4 - 8 hours 225 days per annum	No	41

[Tekst - Slet ikke efterfølgende linje, sektionsskifte]

Substitution of NMP in paint for hard PVC

N-methyl-2-pyrrolidone (NMP) is used in paint to increase the adhesion but NMP is a substance of very high concern due to its negative effects on the human health. Therefor possible alternative solvents have been identified using the software 'Hansen Solubility Parameters in Practice' and evaluated with respect to technical performance, assessed regarding price and commercial availability as well as evaluated with respect to hazard and risk of exposure. Three solvents showed excellent technical performance and are considered applicable alternatives to NMP in PVC paint. From an exposure point of view, one solvent is preferred since it shows a lower risk with respect to inhalation and dermal exposure. However, this solvent has a limited commercial availability and a higher price than both NMP and the other two alternatives. To bring the solutions to marked, development work continues at Teknos in order to document the long-term performance of the product containing the substitute.

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