Ministry of Environment and Food of Denmark
Environmental Protection Agency

Substitution of solvents in printing inks

A project supported by Kemi i Kredsløb

Environmental Project No. 2015

May 2018

Publisher: The Danish Environmental Protection Agency

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ISBN: 978-87-93710-27-6

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1. Foreword

The project “Substitution of solvents in printing inks” was funded by the Danish Environmental Protection Agency’s partnership ‘Kemi i Kredsløb’ and was carried out in the period from April 2017 to March 2018.

This report describes the motivation for the project, the methodology applied and the results achieved during the project period. The aim of the project was to substitute the solvents: methyl ethyl ketone (denoted MEK), toluene and extraction benzine b.p. 100-140 °C (denoted benzine 100-140) used in specific printing inks.

The project was carried out in an interdisciplinary collaboration between Resino Printing Inks A/S, Danish Technological Institute (DTI), DHI and RISE – Research Institute of Sweden. The project management was undertaken by Lars H. Jepsen (DTI), with significant contributions on various levels from Niels Nielsen, Poul Erik Stenfeldt and Karina Nyman (Resino Printing Inks), Tina Slothuus (DHI), Martin Andersson (RISE) and Morten G. Madsen (DTI). Dorte Bjerregard Lerche has followed and approved the project on behalf of the Danish Environmental Protection Agency (EPA).

2. Conclusion and summary

The project deals with the substitution of the three solvents: methyl ethyl ketone (MEK), toluene and extraction benzine b. p. 100-140 °C. Today, these solvents are used to dissolve specific binders in printing inks, but are of concern due to negative effects on the human health and the environment.

In this project, alternative solvents were identified and tested experimentally for four different binders.

Main results

In order to identify alternative solvents with the desired properties, the software Hansen Solubility Parameters in Practice ("HSPiP") was used. By using HSPiP, solvents were intelligently selected for tests in the laboratories based on the theoretical output from the software. The software showed excellent correlation between theory and practice, and is therefore considered a valuable tool to identify alternative solvents. It speeds up the process and saves working hours from typical trial-and-error based approaches.

For three out of the four binders, alternative solvent combinations were identified that performed excellently in the laboratory tests (i.e. they fulfil all technical requirements) and have improved health/environment profiles compared to the solvents currently in use. The solvent cyclopentyl methyl ether (CPME) is part of the solvent combinations for all three binders. However, at the time of writing, the use of this solvent in production has not been possible. The main obstacle is that only a high grade of CPME is available within EU, leading to an unacceptably high price, while a technical grade would be more sufficient for the present purpose. Hence, the solutions have not yet been fully implemented and tested with Resino Inks' customers.

As a side-effect, the solvent dimethyl carbonate was identified as a part of the project. Dimethyl carbonate is a readily biodegradable commodity chemical with good solubility power and has no classifications addressing neither human health nor the environment. Hence, dimethyl carbonate may be used to substitute unwanted chemicals in some of Resino Inks' other recipes than the ones investigated in the current project. However, this has not been investigated further yet, as it was not within the scope of the present project.

3. Konklusion og sammenfatning

Nærværende projekt omhandler substitution af de tre solventer metyletylketon (MEK), toluen og ekstraktionsbenzin kp. 100-140 °C. Disse solventer anvendes i dag til at opløse specifikke bindemidler i trykfarver, men er uønskede grundet negative indflydelser på arbejdsmiljø og sundhed.
I projektet blev der identificeret alternative solventer, som også blev testet eksperimentelt i laboratoriet, for fire forskellige bindemidler.

Hovedresultater
Til at identificere alternative solventer med ønskede tekniske egenskaber blev softwaret *Hansen Solubility Parameters in Practice* ("HSPiP") anvendt. Brugen af softwaret resulterer i en liste af solventer, der teoretisk lever op til de tekniske krav, og baseret på denne liste var det i projektet muligt intelligent at vælge solventer til eksperimentelle tests. HSPiP viste overbevisende sammenhæng mellem teori og praksis, og værktøjet anses derfor for at være et værdifuldt værktøj til at identificere alternative solventer. Identifikationsprocessen går hurtigere, og der kan sparres mange arbejdstimer sammenlignet med traditionel *trial and error* baserede tilgange.

For tre af de fire undersøgte bindemidler blev der identificeret solventkombinationer, der opfylder alle tekniske krav og yder optimalt i laboratorietestene, og som har forbedret miljø- og sundhedsprofiler sammenlignet med solventerne, der anvendes i dag. Solventet cyklopentylmetyleter (CPME) er en del af solventkombinationerne for alle tre bindemidler. På nuværende tidspunkt, har den fulde implementering af CPME i produktionen hos Resino Trykfarver ikke fundet sted endnu, da tilstrækkelig store mængder CPME ikke er blevet leveret til virksomheden. Den primære udfordring for leveringen er, at der i øjeblikket i EU kun er en meget høj kvalitet af CPME tilgængelig, hvilket giver anledning til en uacceptabel høj pris. For Resino vil en teknisk kvalitet til en lavere pris være optimal.

Som en sidegevinst i projektet blev solventet dimetylkarbonat identificeret. Dimetylkarbonat er bionedbrydelig, relativt billig, har en god opløsningsevne og har ingen klassificeringer, der vedrører miljø og sundhed. Dimetylkarbonat kan således blive anvendt i fremtidigt udviklingsarbejde i nogle af Resino Trykfarvers andre trykfarver til at substituere uønskede solventer. Dog var dette arbejde ikke inden for fokus i nærværende projekt.

4. Introduction

Resino Printing Inks specializes in developing inks for print on difficult substrates, e.g. PVC, and inks for general use in printing on packaging. Resino Inks is a world leader in the development of printing inks for printing on sausage casings and has a strong position with inks for food packaging. As an innovative and environmentally conscious company, Resino Inks is continuously working on substitution of undesired chemicals in their products in order to reduce the use of classified chemicals. In this project, the focus was to substitute the solvents methyl ethyl ketone (MEK), toluene and extraction benzine 100-140 °C used in specific printing inks. Among other solvents, MEK is used to dissolve the binders denoted Binder 1 and 2, benzine 100-140 is used to dissolve Binder 3, while toluene is used to dilute a binder denoted Binder 4. Hence, substitution was being investigated for four printing inks:

Binder 1 (problem: MEK)
Binder 2 (problem: MEK)
Binder 3 (problem: Benzine 100-140)
Binder 4 (problem: Toluene)

Resino Inks experiences a significant increase in demand of products with reduced impact on human health and environment, both from customers and legislation. A successful substitution of MEK would enhance the work environment remarkably at both Resino Ink's own factory and at their customers' factories, and is expected to lead to an increased annual turnover in EU and Asia of 1 m and 5 m DKK, respectively. The presence of benzine 100-140 in Binder 3 and toluene in Binder 4 drastically limits the application areas of the binders. Hence, with a substitution of benzine 100-140 and toluene, the two binders can be applied more widespread due to compliance with local working environment demands, leading to expected increase in annual turnovers of 4-5 mio. and 1 mio. DKK, respectively, in relation to export. The specific increase in the profit depends on the expenses to the new solvent(s).

5. Methods

5.1 Strategy to identify alternatives

In order to identify alternative solvents, the substitution process ('Belsutningstræet') described on Kemi i Kredsløb's web page was followed.[1] First, a list with requirements was established, including technical requirements, prices and impact on health and environment (H&E). Subsequently, alternatives were suggested theoretically based on the HSPiP software (see section 5.2). The HSPiP software contains an extensive list of various solvents, but only solvents that fulfil all technical requirements were included. The optimization in the HSPiP software results in a list of alternative solvent combinations that were reviewed quickly with respect to health/environmental impact, expected price and availability. Based on the review, solvent combinations were selected for initial tests in the lab. For positive experimental results, in-depth health/environmental evaluations were carried out and contact to potential suppliers was established. The final step was full tests at Resino Ink as well as at Resino Inks' customers. If solvent combinations failed in one of the steps, previous steps were repeated, typically by new optimizations in the HSPiP software, providing new lists of alternative solvents. Hence, the process consists of numerous iterations between the different steps, aiming at an efficient and goal-oriented process, where both technical, health/environmental and economic aspects were taken into account. The process is illustrated in Figure 1.

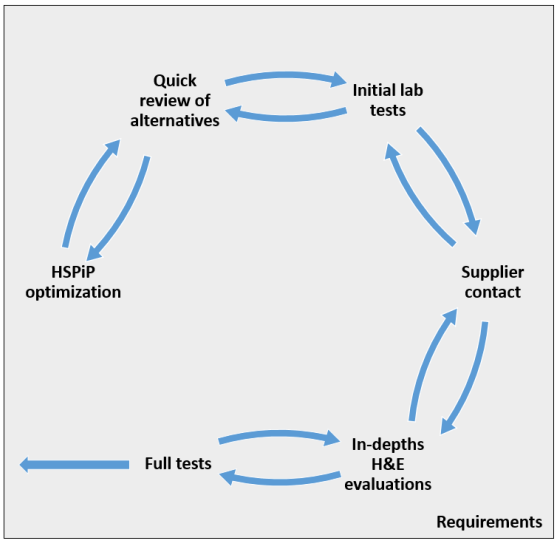


Figure 1 Illustration of the development process

5.2 Hansen solubility parameter

In the project, the Hansen solubility parameters were used in order to predict good solvents for the binders in question. The 'Hansen-tool' is one of the tools described on Kemi i Kredsløbs webpage.[2] The Hansen solubility parameters can describe most solvents and binders in terms of three parameters: The dispersion force D (sometimes called induced-dipole forces, London Forces, London Dispersion forces, or van der Waals forces), the dipolar intermolecular force P and the hydrogen bonding force H. The parameters are then used on the basis that "like dis-

[1] http://web.kemiikredsloeb.com/login/index.php

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

solves like". Meaning a solvent with similar Hansen parameters compared to a binder is expected to dissolve the binder. Mixing two solvents results in a mixed solvent with Hansen parameters in between the two solvents. Meaning that two solvents, when used separately, cannot dissolve a binder, but can dissolve the same binder when mixed in the right proportion.

As it would be prohibitively time-consuming to find the optimal combinations of solvents manually, this feature has been programmed in the software making the process of determining optimal solvent mixtures considerably easier.

Practically, two steps have taken place in this project, where the software Hansen Solubility Parameters in Practice ("HSPiP") was used[3]:

i. Determination of the Hansen solubility parameters (HSP) of the binders
ii. Optimization of solvent combinations giving similar parameters to the binders

The software already contains HSP for several binders. However, the best parameters are achieved by determining them experimentally. The experiment consists of trying to dissolve the binder in a series of different solvents and tracking how well it dissolves. The most accurate HSPs are achieved when many (>10) solvents are used, and when the solvents are as structurally different as possible. That means, as an example, that very little is gained from using both 1-propanol, 1-butanol and 1-pentanol, whereas 1-propanol, heptane and toluene is a better combination. The results from the many solubilities tests in various solvents are given as an input to the software that subsequently calculates the HSP for the binder. Figure 2 illustrates how this is taken place in the HSPiP software. The used solvents are shown in the top left, with the "Score" being the result of the experiment. 1 means that the binder dissolves, and 0 means that the binder does not dissolve. From the combination of good and bad solvents, the Hansen parameters for the binder can be estimated. The estimation is visualized as a green sphere on the lower right. The position of the binder is shown in "Hansen space", where the three parameters (D, P, H) are used as axes. Blue spheres indicate good solvents, while red boxes indicate poor solvents.

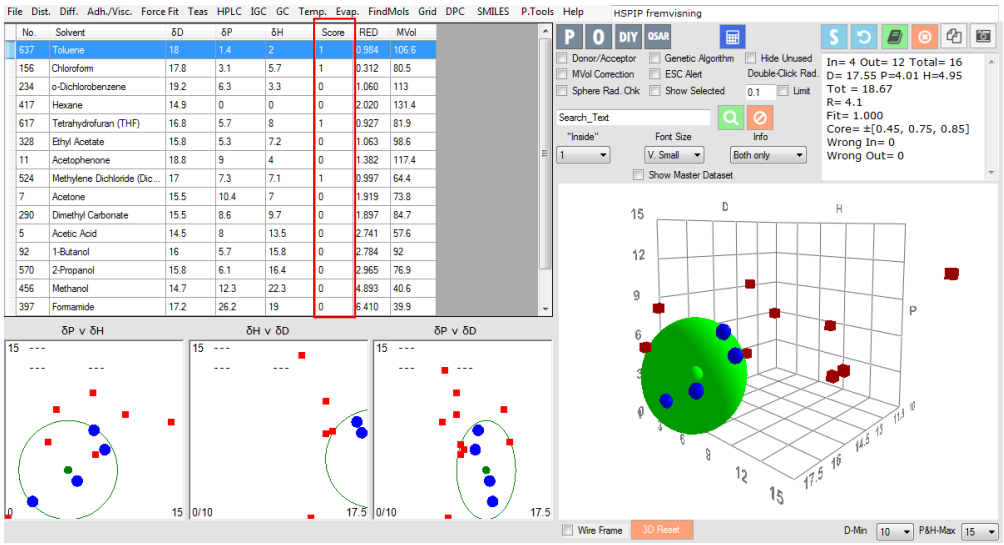


Figure 2: The solubility of a certain binder has been tested in a range of different solvents (toluene, chloroform, etc.) and based on the solubility results (score), the Hansen parameters are determined for the binder.

[3] https://www.hansen-solubility.com/HSPiP/

When the HSP for the binder is determined, it is now possible to calculate combinations of solvents that have similar parameters, and are therefore expected to be able to dissolve the binder. The distance in Hansen space between the solvents and the binders is reported by the RED (Relative Energy Difference) value, where low RED values reflect good solubilities (see Figure 3). Hence, using the list in Figure 3, it can be seen that cyclopentyl methyl ether is expected to be a good solvent (RED value <0.50), while most other solvents from the list are expected to be poor solvents.

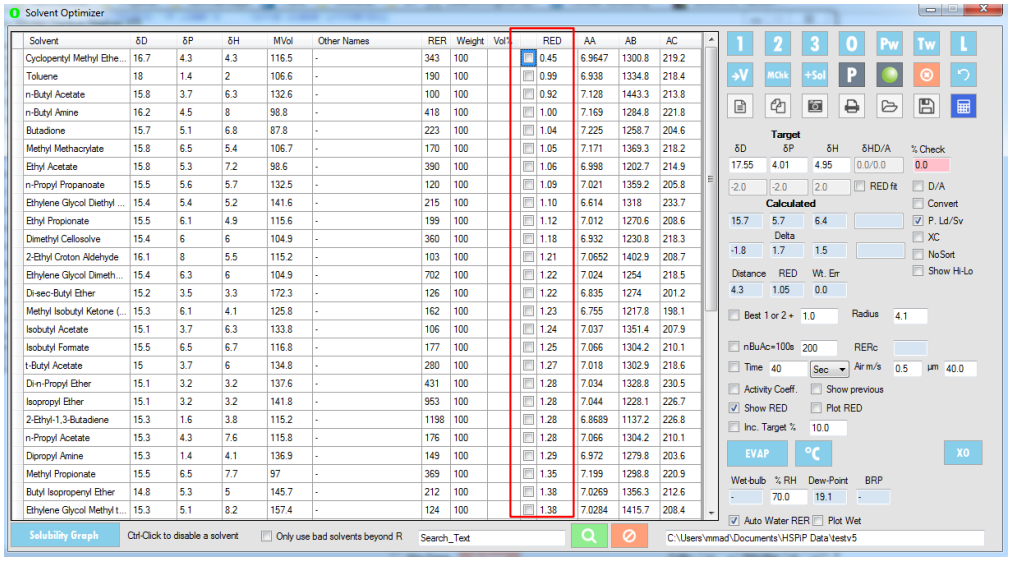


Figure 3: HSPiP solvent optimization. Low RED values reflect good solubilities.

Instead of looking only at single solvents, it is possible to calculate combinations of more solvents, which give better/optimal solubility properties/positions in the Hansen space. The result of using the HSPiP software is a list of solvents or solvent combinations with theoretical solubility properties. Based on the list, the user should consider safety, economic and environmental concerns before selecting solvents for experimental tests.

5.3 Health and environmental evaluation

The three solvents currently used at Resino Inks and those solvents, which were considered as possible candidates for replacing the three solvents, were evaluated with respect to possible concerns of environmental and human health effects. Publicly available databases were consulted, and information was collected with respect to classification, eco-toxicity (both acute and chronic data on the toxicity towards algae, invertebrate, and fish) and environmental fate (including biodegradation and potential for bioaccumulation). Furthermore, the REACH candidate list, the Substitute It Now List (SIN-List) and EU's list of endocrine disrupters were consulted in order to avoid substances with undesired properties. The SIN List is developed by ChemSec and it should be noted that the SIN-List is a database of both problematic and potentially problematic substances, either on the REACH lists (including the candidate list, authorization list, restriction list, CoRAP lists, full registration and intermediate registration) or problematic according to REACH's criteria for hazardous.

5.4 Laboratory tests

Using the solvent combinations suggested by the HSPiP software, a series of test inks were prepared in the laboratory at Resino Inks. The test inks were prepared using the same recipes

as commercial recipes, except for the change in solvents. The recipes contained the binders, pigments, and for some of the systems small amounts of film-improving compounds.

Subsequently, the test inks were characterized using the same tests as the commercial inks are subjected to during regular quality control. The tests include, among others, viscosity, drying time, tape resistance, color strength tests and stability tests.

The better a binder is dissolved; the lower viscosity is obtained. Hence, the viscosity test is the most critical test as it is a direct measure of the solubility power of the solvents investigated. The viscosity was measured using the Ford viscosity cup method, and the alternative solvents were compared against solvents currently used at Resino Inks. A standardized metal cup is filled to the edge, and the time taken for the ink to flow out through a hole in the bottom is measured. Under ideal conditions, the rate of flow is proportional to the kinematic viscosity (the dynamic viscosity divided by the density of the fluid).

Subsequent to the viscosity test, the inks were applied on different substrates and e.g. the drying time, color and resistance were evaluated. Stability tests were performed by leaving the test inks in cold storage for a given period, and then testing the parameters at various intervals.

6. Requirement specification

6.1 Technical requirements

The boiling point of the alternative solvents should be above 70 °C, and the freezing point should be below -40 °C, or the finished ink should easily be re-mixable after thawing.

The relative evaporation rate should be similar to ethyl acetate and MEK, as the current printing machines are optimized for these solvents, i.e. relative evaporation rate > 150.

6.2 Costs

In order to minimize cost, which is important when considering implementing a new substance in the production, it was determined that a price twice that of the original substance was acceptable for initial screening. This was based on the assessment of market demand, expected increase in market value of a more environmentally friendly product and the balance between total earnings by launching a new product vs. the earning per product.

6.3 Health and environment

The aim of the project was to reduce the health and environmental impact of the solvents. All solvents with poorer classifications as the undesired solvents were filtered out immediately in the screening process. If available, the harmonized classification was applied, if not, the notified classifications was evaluated. In order to avoid regrettable substitution, an in-depth health and environmental analysis was performed on the most promising solvents, selected after the initial screening (see Chapter 9).

The evaporation of the solvents is mainly taken place at Resino's customers where the inks are printed on various products. All larger companies within EU have installed incineration systems that ensure that the solvents are not exposed to the environment. Hence, e.g. the biodegradability of the solvents is of less importance.

7. Identification of alternative solvents

Alternative solvents and solvent combinations were identified for the four binders (Binder 1-4) by using the HSPiP software, see Table 1. Selected alternatives were carried through to experimental tests, see chapter 8.

Table 1 Alternative solvents and solvent combinations identified. DMSO refers to dimethyl sulfoxide, CPME refers to cyclopentyl methyl ether and MTBE refers to methyl tert-butyl ether.

	Sample no	Solvent 1	Solvent 2	vol% 1	vol% 2	Selected for test	Comments
Binder 1	**1**	1,3-Dioxolane	-	100	-	Yes	
	2	DMSO	-	100	-	Yes	
	3	Dimethyl carbonate	-	100	-	Yes	
	4	Ethyl acetate	Dimethyl carbonate	38	62	Yes	
	5	CPME	Dimethyl carbonate	48	52	Yes	
	6	Acetonitrile	Dimethyl carbonate	20	80	Yes	
	7	CPME	-	100	-	Yes	
	8	CPME	Acetonitrile	68	32	Yes	
	9	CPME	1,3-dioxolane	77	23	Yes	
	10	CPME	Dimethyl carbonate	89	11	Yes	
	11	MTBE	-	100	-	Yes	
	12	CPME	Dimethyl carbonate	61	39	Yes	
	13	Ethyl propionate	Ethyl acetate	40	60	Yes	
	14	Ethyl propionate	Ethanol	90	10	No	Attempted previously by Resino Inks.
	15	Ethyl propionate	2-propanol	88	12	Yes	
	16	n-propyl propionate	Ethyl acetate	40	60	Yes	
	17	Ethyl propionate	Ethyl formate	68	32	No	Ethyl formate too expensive.
Binder 2	**21**	1,3-dioxolane	Acetonitrile	75	25	Yes	
	22	CPME	Acetonitrile	68	32	Yes	
	23	1,3-dioxolane	CPME	67	33	Yes	
	24	1,3-dioxolane	-	100	-	Yes	
	25	CPME	Dimethyl carbonate	70	30	Yes	
	26	Ethyl acetate	MTBE	93	7	Yes	
Binder 3	**31**	2-propanol	-	100	-	Yes	
	32	2-propanol	Ethyl acetate	73	27	Yes	
	33	2-propanol	MTBE	80	20	Yes	
	34	2-propanol	CPME	79	21	Yes	

	35	2-propanol	Di-n-propyl ether	82	18	No	Di-n-propyl ether too expensive.
	36	2-propanol	Propyl formate	72	28	Yes	
	37	2-propanol	Methyl propionate	74	26	Yes	
	38	2-propanol	Ethyl butyl ether	81	19	No	Ethyl butyl ether too expensive.
	39	2-propanol	t-butyl acetate	78	22	No	t-butyl acetate has an unpleasant odor.
Binder 4	**41**	CPME	-	100	-	Yes	
	42	CPME	1,3-Dioxolane	87	13	Yes	
	43	MTBE	-	100	-	Yes	
	44	MTBE	Toluene	40	60	Yes	
	45	MTBE	1,3-Dioxolane	51	59	Yes	
	46	n-butyl acetate	-	100	-	No	n-butyl acetate has an unpleasant odor.
	47	Ethyl acetate	-	100	-	No	Attempted by Resino Inks before project start.

8. Experimental tests

Selected alternative solvent combinations from Table 1 were tested experimentally with respect to viscosity, nail resistance, tape resistance, color (shade, gloss and strength), drying time, grinding and adhesion to PVC, see Table 2 to 5.

- The viscosity is a direct measure for how well a binder is dissolved by the solvents.
- Nail resistance is a measure of the ink's behavior towards scratching and reflects the cohesion of the ink.
- Tape resistance measures the ink adhesion to the substrate.
- Color tests are measures of the look.
- Drying time measures the time before the ink is sufficiently dry.
- Grinding tests ensure that the pigment is properly dispersed during production.
- Adhesion to PVC tests focuses on the adhesion towards PVC, which is especially challenging.

The effect of the Hansen solubility parameters can be seen by comparing sample no 3, 5 and 7 in Table 2. For pure dimethyl carbonate (no. 3) and pure CPME (no. 7), the viscosities are 5 minutes and 90 seconds, respectively, while when mixing the two solvents (no. 5), the viscosity was lowered to 65 seconds. In order words, two solvents, when used separately, dissolve a binder poorly, but dissolve the same binder better when mixed in the right proportion.

The aim for Binder 1 was to achieve a viscosity of 27-33 seconds, similar to the reference sample with methyl ethyl ketone. However, despite the effect of improving the solubility by mixing solvents, the best achieved viscosity was 55 seconds for the investigated solvent combinations (no 9). Hence, it was not possible to meet this demand within the defined criteria.

Table 2 Solvent tests for Binder 1. The first row with methyl ethyl ketone (MEK) is the reference, which all other solvent combinations were compared to. A result of 'OK' means that the sample passed the test. DMSO refers to dimethyl sulfoxide, and CPME refers to cyclopentyl methyl ether.

Solvent	Sample no.	Viscosity DIN4 27-33sec	Nail resistance	Tape resistance	Color shade	Drying time sec	Grinding	Color gloss visual	Color strength visual	PVC adhesion
Methyl ethyl ketone	Reference	27 sec	OK	OK	OK	15	OK	OK	OK	OK
1,3-Dioxolane	1	Ca. 3 min	NOT OK	NOT OK	OK	20	-	OK	NOT OK	-
DMSO	2	Ca. 3,5 min	NOT OK	NOT OK	OK	120	-	NOT OK	NOT OK	-
Dimethyl carbonate	3	Ca. 5 min	NOT OK	NOT OK	OK	25	-	OK	NOT OK	-
Ethyl acetate/ Dimethyl carbonate 38/62	4	60 sec	NOT OK	NOT OK	NOT OK	15	OK	NOT OK	OK	NOT OK
Dimethyl carbonate/CPME 52/48	5	65 sec	OK	OK	NOT OK	20	OK	OK	OK	OK
Dimethyl carbonate/ Acetonitrile 80/20	6	120 sec	OK	OK	NOT OK	15	OK	OK	OK	OK
CPME	7	90 sec	OK	OK	OK	17	OK	OK	OK	OK

Solvent	Sample no.	Viscosity DIN4 27-33sec	Nail re-sistance	Tape re-sistance	Color shade	Drying time sec	Grind-ing	Color gloss visual	Color strength visual	PVC adhe-he-sion
CPME/Acetonitrile 79/21	8	90 sec	OK	OK	OK	20	OK	OK	OK	OK
CPME/1,3-dioxolane 77/23	9	55 sec	OK	OK	OK	20	OK	OK	OK	OK
CPME/ Dimethyl carbonate 89/11	10	65 sec	OK	OK	OK	17	OK	OK	OK	OK
MTBE	11	Pigment can't dissolve	-	-	-	-	-	-	-	-
CPME/ Dimethyl carbonate 56/44	12	65 sec	OK	OK	OK	23	OK	OK	NOT OK	OK
Ethyl propionate/ethyl acetate 40/60	13	120 sec	OK	OK	NOT OK	25	OK	OK	OK	OK
Ethyl propionate/2-propanol 88/12	15	>90 s	NOT OK	OK	NOT OK	19	OK	OK	NOT OK	OK
n-Propyl propionate/ethyl acetate 38/62	16	>65 s	NOT OK	NOT OK	NOT OK	21	NOT OK	OK	NOT OK	OK

For Binder 2, it was found that three of the solvent combinations passed all tests (no 21, 25 and 26, Table 3). Subsequently, two of the combinations were discarded (no 21 and 26), when it was apparent that MTBE is classified as an endocrine disrupter, and 1,3-dioxolane has an unacceptable odor.

Table 3 Solvent tests for Binder 2. CPME refers to cyclopentyl methyl ether.

Solvent	Sample no.	Results
1,3-dioxolane/acetonitrile 75/25	21	Solubility ok, but disagreeable odor, and too high price.
CPME/Acetonitrile 68/32	22	Acetonitrile is too expensive.
1,3-dixolane/CPME 67/33	23	Tape test failed.
1,3-dixolane 100	24	Disagreeable odor.
CPME/dimethyl carbonate 70/30	25	OK
Ethyl acetate/MTBE 93/7	26	OK. Discarded due to MTBE being endocrine disrupting.

For Binder 3, three solvent combinations passed all initial tests (sample no 34, 36 and 37, Table 4). An additional test was carried out, as these inks are known to destabilize over time. Therefore, the samples that initially passed all tests were tested again every month for three months. Here, sample no 37 failed the stability test after two months, while sample no 34 and 36 remained stable.

Table 4 Solvent tests for Binder 3. CPME refers to cyclopentyl methyl ether, and MTBE refers to methyl tert-butyl ether.

Solvent	Sample no.	Results
2-propanol 100	31	Not OK
2-propanol/ethyl acetate 73/27	32	Not OK
2-propanol/MTBE 80/20	33	Not OK
2-propanol/CPME 79/21	34	OK, stable after 3 months
2-propanol/propyl formate 72/28	36	OK, stable after 3 months
2-propanol/methyl propionate 74/26	37	Initially OK, fails stability test after 2 months.

For Binder 4, the technical demands were slightly less strict, and consequently, all five tested solvent combinations passed the technical tests, see Table 5.

Table 5 Solvent tests for Binder 4. CPME refers to cyclopentyl methyl ether, and MTBE refers to methyl tert-butyl ether.

Solvent	Sample no.	Results
CPME 100	41	OK
CPME/1,3-Dioxolane 87/13	42	OK, disagreeable odor
MTBE 100	43	OK
MTBE/Toluene 40/60	44	OK
MTBE/1,3-dioxolane 51/49	45	OK, disagreeable odor

9. Substance profiles - Environment and Human Health

Current solvents and all solvents, which were considered as possible alternatives, were evaluated with respect to possible concerns towards the environment and human health. Substance profiles were evaluated for both existing substances, methyl ethyl ketone (MEK), toluene and benzine 100-140 and for alternative substances. Results are presented in Appendix A, where environmental and human health factors, which are a problem with the current substances or that may cause alternative substances to be unsuitable candidates for substitution, are highlighted in red.

9.1 Current solvents

Methyl ethyl ketone (MEK) has a bad smell, which is why Resino Inks would like to find an alternative for their customers.

Toluene is classified with H361d (Suspected of damaging the unborn child) and is therefore considered a candidate for substitution.

Extraction benzine b.p. 100-140 °C is classified with H350 (may cause cancer) and is therefore considered a candidate for substitution. However, according to Regulation 1272/2008 (note P), this classification only applies if the concentration of benzene is above >0.1%. A possible solution, which would still allow the use of benzine 100-140, is to purchase a product with a benzene content below 0.1%. If such a product would still be applicable, as a solvent was not evaluated within this project.

9.2 Alternative substances

The following section enlists the substances, which were considered as possible alternatives, with a more in-depth discussion of the environmental and human health effects. Appendix A presents the full overview of the evaluated substances within this project.

MTBE, in addition to being price competitive, is found to be a good solvent for several binders. Thus, the solvent could contribute to the substitution of all three solvents MEK, benzine 100-140 and toluene. However, MTBE might have potential endocrine properties, i.e. MBTE can interfere with the endocrine (or hormone) systems and was thus initially included on the EU priority list where it was listed as a Category 1 chemical. The list does not exist anymore, but has been replaced with an EU-database which is publically available. The substances on the EU-database still need to be further examined with respect to their endocrine properties; however, several studies are available indicating the endocrine properties of MTBE and justifying the classification as a category 1 chemical.
MTBE is also included on the CoRAP list due to its potential endocrine disrupting effects, a high (aggregated) tonnage and a wide dispersive use as an additive to car fuel. The substance evaluation decision also states concerns regarding mutagenic effects, and also concludes, that further information is required including studies on the endocrine disrupting properties (OECD Guideline no. 234, “Fish Sexual Development Test”) and a transgenic rodent somatic and

germ cell gene mutation assays (TGR) (OECD TG 488) before any final conclusions can be drawn.

Furthermore, and specifically relevant since the inks are used for food contact materials is that MTBE has an unpleasant odor and taste even at extremely low concentrations. MBTE was therefore disregarded as a possible alternative substance and no further work was performed on this substance during the project.

CPME is not readily biodegradable (perhaps inherently not biodegradable based on QSAR predictions). The highest toxicity is observed towards invertebrates where an EC50 (48h) of 35 mg/L is reported. CPME is not expected to bio-accumulate in the environment (Log Kow = 1.6). The lack of biodegradation and the toxicity justifies the notified classification as H412 (harmful to aquatic life with long-lasting effects) reported in the C&L inventory. The substance is, however, considered acceptable for substitution in the present context if its release to the environment is controlled and kept to a minimum.

Both **Cyclohexane and methyl cyclohexane** are classified for environmental hazard: Cyclohexane: H411 (toxic to aquatic life with long-lasting effects) and methyl cyclohexane: H400 (very toxic to aquatic life) and H410 (very toxic to aquatic life with long-lasting effects). The classification H411 is given to substances (methyl cyclohexane) that are not readily biodegradable and which have an acute toxicity (EC50) of 1-10 mg/L towards aquatic organisms. In the REACH registration, data for methyl cyclohexane indicating an aquatic toxicity EC50 < 1 mg/L were also reported.
The classification H400+H410 is given to substances (cyclohexane) which have a toxicity towards aquatic organisms EC50 ≤ 1 mg/L and which have a potential for bioaccumulation (Log Kow > 4) and/or not ready biodegradable. In the REACH registration, data for cyclohexane indicating readily biodegradability is available.
The substances are considered acceptable for substitution in the present context if the release to the environment is controlled and kept to a minimum.

Dimethyl sulfoxide (DMSO) is not readily biodegradable. However, it is not toxic towards the aquatic environment (EC50 > 1000 mg/L) and has a low potential for bioaccumulation (Log Kow = -1.35). Furthermore, the substance is not classified and not included in any of the assessed list. Therefore, no environmental and human health concerns are identified for this substance, and DMSO is considered acceptable for substitution in the present context.

1,3 Dioxolane, is not readily biodegradable. However, it has a low toxicity towards the aquatic environment (EC50 > 100 mg/L) and has a low potential for bioaccumulation (Log Kow = -0.37). Furthermore, the substance does not have a harmonized classification addressing human health nor the environment (although a notified classification is available where half of the registrants have stated a classification as possible reprotoxic (H360)) and not included in any of the assessed lists. Therefore, no environmental and human health concerns are identified, and the substance is considered acceptable for substitution in the present context, however focus should be kept on a possible change in the classification.

Dimethyl carbonate is readily biodegradable, has a low toxicity towards the aquatic environment (EC50 > 100 mg/L), and a low potential for bioaccumulation (Log Kow = 0.354). Furthermore, the substance has no classifications addressing neither human health nor the environment and it is not included in any of the assessed list. Therefore, no environmental and human health concerns are identified for this substance, and the substance is considered ideal for substitution in the present context.

10. Technical conclusion

During this project, the project participants succeeded in identifying solvent substitutions, which meet the performance goals and fulfil all criteria for three out of the four binders investigated (Binders 2-3-4). The alternative solvents/solvent combinations were identified using the Hansen solubility parameters, subsequently demonstrating value of this tool in combination with the empirical knowledgebase available at Resino Ink.

For Binder 1, 15 alternative solvents/solvent combinations were tested, and none of them lived up to the same high performance as the current solvent combinations including MEK. Hence, it was not possible to obtain an adequate substitution within the defined criteria. A reduction of MEK was not attempted as only a full substitution was desired. Similarly, the substitution with other ketones was not accepted.
For Binder 2, three solvent combinations fulfilled the initial tests, but two of the combinations were discarded due to either odor or health and environmental profiles of the solvents. The third alternative is the combination CPME/dimethyl carbonate 70/30, which fulfils all criteria.
For Binder 3, two solvent combinations passed all experimental tests and was found to have less of an environmental impact compared to the solvents currently used, i.e. 2-propanol/CPME 79/21 and 2-propanol/propyl formate 72/28.

For Binder 4, all five tested solvent combinations passed the technical tests, but only CPME live up to all criteria. Four of the tested alternatives were discarded due to bad odor, and the health and environmental profile of the solvents.

The implementation of the Binder 2-4 including the new solvent combinations into Resino Inks' commercial product portfolio is described in the following paragraph.

Additionally, the biodegradable commodity solvent dimethyl carbonate was identified as part of the project. Dimethyl carbonate is an excellent solvent and has no classifications with respect to the human health or the environment. Dimethyl carbonate may thus be used to substitute other unwanted chemicals in some of Resino Inks' recipes, which was not the focus of the present project.

11. Implementation

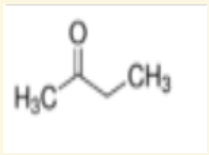
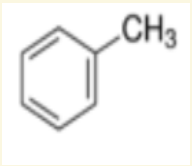
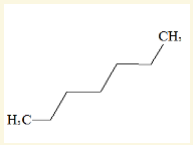
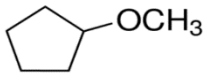
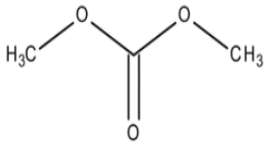
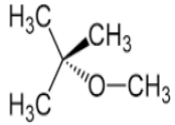
Within the project period, there was a continuous focus on implementation reflected by the requirements defining the frame for the performed work. During the project, Resino Inks have been in contact with some of their customers, who are ready to test the developed printing inks containing the alternative solvents. However, the customer tests have not been performed at the time of writing, as obtaining sufficient amounts of the key solvent CPME have proven challenging. Resino Inks is in a ongoing dialog with suppliers of CPME, but it is currently challenging to acquire large amounts of a technical grade of CPME within EU.

It was not within the scope of the present project to investigate the potential of the green solvent dimethyl carbonate. It has the potential to substitute unwanted chemicals in some of Resino Inks' other recipes, and the solvent will be integrated in Resino Inks' continuous development. Finally, the HSPiP software is being implemented at Resino Ink, enabling faster identifications of more green solvent combinations, as compared to classical trial-and-error based approaches.

12. Appendix A

Data on environmental and human health effects

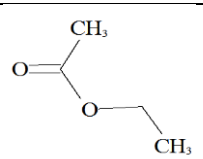
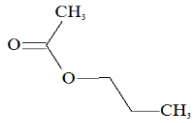
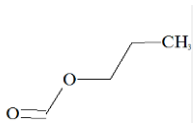
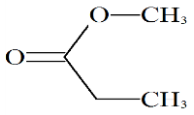
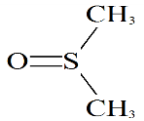
Table A-1: Substance profiles (Environment and human health evaluation). Environmental and health factors, that may cause these substances to be unsuitable alternatives for substitution, are highlighted in red.

Substance	**Methylethylketone (MEK)**	**Toluene**	**Extraction benzine b. p. 100-140 °C**	**CycloPentyl Methyl Ether (CPME)**	**Dimethyl carbonate**	**2-methoxy-2-methylpropane (MTBE)**
CAS	78-93-3	108-88-3	64742-49-0	5614-37-9 (EINECS=445-090-6)	616-38-6	1634-04-4
Structure						
Molecular formula	C2H5COCH3	C6H5CH3	C7H16	C6H12O	C3H6O3	C5H12O
CLP /1/	**Harmonised classification:**	**Harmonised classification:**	**Harmonised classification:**	**Notified classification:**	**Notified classification:**	**Notified classification:**
	H225 (Highly flammable liquid and vapour)	H225 (Highly flammable liquid and vapour)	H304 (May be fatal if swallowed ad enters airways)	H225 (Highly flammable liquid and vapour)	H225 (Highly flammable liquid and vapour)	H225 (Highly flammable liquid and vapour)
	H319 (Causes serious eye irritation)	H304 (May be fatal if swallowed ad enters airways)	H340 (may cause genetic defects)	H302 (Harmful if swallowed)		H315 (Causes skin irritation)
	H336 (May cause drowsiness or dizziness)	H315 (Causes skin irritation)	**H350 (May cause cancer)**	H315 (Causes skin irritation)		
		H336 (May cause drowsiness or dizziness)		H319 (Causes serious eye irritation)		

Substance	Methylethylketone (MEK)	Toluene	Extraction benzine b. p. 100-140 °C	CycloPentyl Methyl Ether (CPME)	Dimethyl carbonate	2-methoxy-2-methylpropane (MTBE)
		H373 (May cause damage to organs)		**H412 (Harmful to aquatic life with long lasting effects)**		
Environmental fate /2,3/	Biodegradation: Ready biodegradable (not P)	Biodegradation: Ready biodegradable (not P)	Biodegradation: NA	**Biodegradation: Not readily biodegradable (Episuite ready. Conclusion: possibly inheret biode.)**	Biodegradation: Ready biodegradable (not P)	**Biodegradation: Not readily biodegradable (P)**
	Log Kow: -0.3 (40°C) (not B)	Log Kow: 2.73 (not B)	Log Kow: NA	Log Kow: 1.6	Log Kow: 0.354	Log Kow: 1.06
Ecotoxicity /2,3/	EC50 (96h, fish) = 2993 mg/L	EC50 (96h, fish) = 5.5 mg/L	LL50 (96h, fish) = 8.2mg/L	LC50 (96h, fish) >220 mg/L	LC50 (96h, fish) ≥100 mg/L	LC50 (96h, fish) = 672 mg/L
	EC50 (48h, inv.) = 308 mg/L	NOEC (40d, fish) = 1.39 mg/L	EL50 (48h, inv.) = 4.5 mg/L	EC50 (48h, inv.) = 35 mg/L	EC50 (48h, inv.) >100 mg/L	NOEC (96h, fish) = 299 mg/L
	ErC50 (72h, algae.) = 1972 mg/L	EC50 (48h, inv.) = 3.78 mg/L	NOEL (21d, inv.) = 2.6 mg/L	ErC50 (72h, algae.) >100 mg/L	NOEC (21d, inv.) = 25 mg/L	EC50 (48h, inv.) = 472 mg/L
	EC10 (72h, algae) =1289 mg/L	**NOEC (7d, inv.) = 0.79 mg/L**	ErC50 (72h, algae.) = 3.1 mg/L	NOEC (72h, algae) = 2.2 mg/L	ErC50 (72h, algae) >100 mg/L	NOEC (21d, inv.) = 26 mg/L
		EC50 (72h, algae.) = 134 mg/L	NOEL (72h, algae) = 0.5 mg/L		NOEC (72h, algae) >100 mg/L	IC50 (72h, algae) = 491 mg/L
						IC20 (72h, algae) = 103 mg/L
PBT	CLP: (Not T)	CLP: H361d (T)	CLP: H350 (T)	CLP: (Not T)	CLP: (Not T)	CLP: (Not T)
	Conclusion: Based on the data above the substance is not a PBT substance	Conclusion: Based on the data above the substance is not a PBT substance	Conclusion: na	Conclusion: Based on the data above the substance is not a PBT substance	Conclusion: Based on the data above the substance is not a PBT substance	Conclusion: Based on the data above the substance is not a PBT substance

Substance	Methylethylketone (MEK)	Toluene	Extraction benzine b. p. 100-140 °C	CycloPentyl Methyl Ether (CPME)	Dimethyl carbonate	2-methoxy-2-methylpropane (MTBE)
vPvB	Conclusion: Based on the data above the substance is not a vPvB substance	Conclusion: Based on the data above the substance is not a vPvB substance	Conclusion: na	Conclusion: Based on the data above the substance is not a vPvB substance	Conclusion: Based on the data above the substance is not a vPvB substance	Conclusion: Based on the data above the substance is not a vPvB substance
Endocrine Disrupting Chemical (EDC) /4, 5, 6/	Not included /4, 5, 6/	Not included /4, 5, 6/	Not included /4, 5, 6/	Not included /4, 5, 6/	Not included /4, 5, 6/	Not included /4/ **Included /5, 6/ CAT1 (human health) and CAT2 (wildlife). Overall assessment = CAT1***
VOC /2/ (Bp< 250 °C)	Bp = 79.59 °C (1 atm) **Conclusion: Volatile**	Bp= 110.6°C (1atm) **Conclusion: Volatile**	Bp= 58 °C (1atm) **Conclusion: Volatile**	Bp = 107 °C (1atm) **Conclusion: Volatile**	Bp = 90 °C (1atm) **Conclusion: Volatile**	Bp = 55.3 °C (1atm) **Conclusion: Volatile**
Substitute It Now (SIN list) /7/	Not included	Not included	**Included (due to classi-fication)**	Not included	Not included	**Included (due to EDC)**
REACH Candidate list/SVHC /8/	Not included	Not included	Not included	Not included	Not included	Not included
EU list of allergenic substanc-es /9/	Not included	Not included	Not included	Not included	Not included	Not included

Table A-1: Substance profiles (Environment and human health evaluation). Environmental and health factors, that may cause these substances to be unsuitable alternatives for substitution, are highlighted in red. (continued)

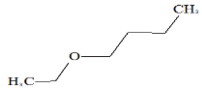
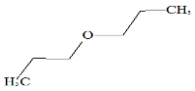
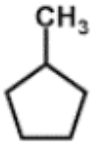
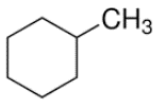
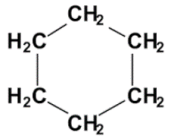
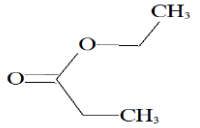
Substance	**Ethyl acetate**	**n-propyl acetate**	**Propyl formate**	**Methyl propionate**	**Dimethyl sulfoxide**	**1,3-Dioxolane**
CAS	**141-78-6**	**109-60-4**	**110-74-7**	**554-12-1**	**67-68-5**	**646-06-0**
Molecular formula	C4H8O2	C5H10O2	C4H8O2	C4H8O2	C2H6OS	C3H6O2
Structure						
CLP /1/	**Harmonised classification:**	**Harmonised classification:**	**Harmonised classification:**	**Harmonised classification:**	**Not classified**	**Harmonised classification:**
	H225 (Highly flammable liquid and vapour)	H225 (Highly flammable liquid and vapour)	H225 (Highly flammable liquid and vapour)	H225 (Highly flammable liquid and vapour)		H225 (Highly flammable liquid and vapour)
	H319 (Causes serious eye irritation)	H319 (Causes serious eye irritation)	H319 (Causes serious eye irritation)	H332 (Harmful if inhaled)		
	H336 (May cause drowsiness or dizziness)	H336 (May cause drowsiness or dizziness)	H335 (May cause respiratory irritation)			
			H336 (May cause drowsiness or dizziness)			
Environmental fate /2, 3/	Biodegradation: Ready biodegradable (not P)	Biodegradation: Ready biodegradable (not P)	Biodegradation: Ready biodegradable (Not P) /10/	Biodegradation: Ready biodegradable (Not P) /10/	**Biodegradation: Not readily biodegradable (P)**	**Biodegradation: Not readily biodegradable (P)**
	Log Kow: 0.68	Log Kow: 1.4	Log Kow: 0.83 /10/	Log Kow: 0.86 /10/	Log Kow: -1.35	Log Kow: -0.37

Substance	Ethyl acetate	n-propyl acetate	Propyl formate	Methyl propionate	Dimethyl sulfoxide	1,3-Dioxolane
Ecotoxicity /2, 3/	LC50 (96h, fish) = 220 mg/L	LC50 (96h, fish) = 60 mg/L	LC50 (96h, fish) = 57 mg/L /10/	LC50 (96h, fish) = 53 mg/L /10/	LC50 (96h, fish) >25000 mg/L	LC50 (96h, fish) >95,4 mg/L
	EC50 (24h, inv.) 3090 mg/L	EC50 (48h, inv.) 91.5 mg/L			EC50 (48h, inv.) = 24600 mg/L	EC50 (48h, inv.) > 772 mg/L
	NOEC (72h, algae) >100 mg/L	EC50 (72h, algae) = 672 mg/L			EC50 (72h, algae) = 17000 mg/L	EC50 (72h, algae) >872 mg/L
	NOEC (72h, algae) >100 mg/L	NOEC (72h, algae) = 83.2 mg/L				
PBT	CLP: Not T	CLP: Not T	CLP: Not T	CLP: Not T	CLP: Not T	CLP: Not T
	Conclusion: Based on the data above the substance is not a PBT substance	Conclusion: Based on the data above the substance is not a PBT substance	Conclusion: Based on the data above the substance is not a PBT substance	Conclusion: Based on the data above the substance is not a PBT substance	Conclusion: Based on the data above the substance is not a PBT substance	Conclusion: Based on the data above the substance is not a PBT substance
vPvB	Conclusion: Based on the data above the substance is not a vPvB substance	Conclusion: Based on the data above the substance is not a vPvB substance	Conclusion: Based on the data above the substance is not a vPvB substance	Conclusion: Based on the data above the substance is not a vPvB substance	Conclusion: Based on the data above the substance is not a vPvB substance	Conclusion: Based on the data above the substance is not a vPvB substance
Endocrine Disrupting Chemical (EDC) /4, 5, 6/	Not included /4, 5, 6/	Not included /4, 5, 6/	Not included /4, 5, 6/	Not included /4, 5, 6/	Not included /4, 5, 6/	Not included /4, 5, 6/
VOC /2/ (Bp< 250 °C)	Bp = 77.1 °C (1atm)	Bp = 101.5 °C (1atm)	Bp = 80.9 °C (1atm) /10/	Bp = 79.8 °C (1atm) /10/	Bp = 189 °C (1atm)	Bp = 76°C (1atm)
	Conclusion: Volatile	**Conclusion: Volatile**	**Conclusion: Volatile**	**Conclusion: Volatile**	**Conclusion: Volatile**	**Conclusion: Volatile**
Substitute It Now (SIN	Not included	Not included	Not included	Not included	Not included	Not included

Substance	Ethyl acetate	n-propyl acetate	Propyl formate	Methyl propionate	Dimethyl sulfoxide	1,3-Dioxolane
list) /7/						
REACH Candidate list/SVHC /8/	Not included	Not included	Not included	Not included	Not included	Not included
EU list of allergenic substances /9/	Not included	Not included	Not included	Not included	Not included	Not included

Table A-1: Substance profiles (Environment and human health evaluation). Environmental and health factors, that may cause these substances to be unsuitable alternatives for substitution, are highlighted in red. (continued)

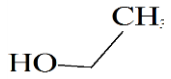
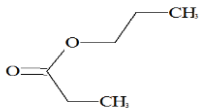
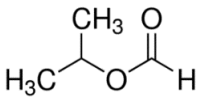
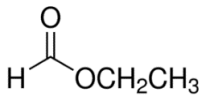
Substance	Ethyl Butyl Ether	Di-n-Propyl Ether	Methyl Cyclopentane	Methyl Cyclohexane	Cyclohexane	Ethyl propionate

Substance	Ethyl Butyl Ether	Di-n-Propyl Ether	Methyl Cyclopentane	Methyl Cyclohexane	Cyclohexane	Ethyl propionate
CAS	**628-81-9**	**111-43-3**	**96-37-7**	**108-87-2**	**110-82-7**	**105-37-3**
Molecular formula	C6H14O	C6H14O	C6H12	C6H11CH3	C6H12	C5H10O2
Structure						
CLP /1/	**Notified classification:**	**Notified classification:**	**Notified classification:**	**Harmonised classification:**	**Harmonised classification:**	**Harmonised classification:**
	H225 (Highly flammable liquid and vapour)	H225 (Highly flammable liquid and vapour)	H315 (Causes skin irritation)	H225 (Highly flammable liquid and vapour)	H225 (Highly flammable liquid and vapour)	H225 (Highly flammable liquid and vapour)
	H302 (Harmful if swallowed)	H336 (May cause drowsiness or dizziness)	H319 (Causes serious eye irritation)	H304 (May be fatal if swallowed ad enters airways)	H304 (May be fatal if swallowed ad enters airways)	
			H335 (May cause respiratory irritation)	H315 (Causes skin irritation)	H315 (Causes skin irritation)	
				H336 (May cause drowsiness or dizziness)	H336 (May cause drowsiness or dizziness)	
				H411 (Toxic to aquatic life with long lasting effects)	**H400 (Very toxic to aquatic life)**	
					H410 (Very toxic to aquatic life with long lasting effects)	
Environmental fate /2, 3/	Biodegradation: Ready biodegradable (Not P)	Biodegradation: Ready biodegradable (Not P) /10/	Biodegradation: Ready biodegradable (Not P)	**Biodegradation: Not readily biodegradable (P)**	Biodegradation: Ready biodegradable (not P)	Ready biod. /10/

Substance	Ethyl Butyl Ether	Di-n-Propyl Ether	Methyl Cyclopentane	Methyl Cyclohexane	Cyclohexane	Ethyl propionate
	/10/		/10/			
	Log Kow: 2.03 (exp. data)	Log Kow: 2.03 (exp. data)	Log Kow: 3.1 /10/	Log Kow: 3.88	Log Kow: 3.44	Log Kow: 1.21 (exp.) /10/
Eco-toxicity /2, 3/	EC50 (96h, algae) = 20 mg/L /10/	EC50 (96h, algae) = 20 mg/L /10/	EC50 (96h, algae) = 3,536 mg/L /10/	LC50 (96h, fish) = 2,07 mg/L	LC50 (96h, fish) = 4,53 mg/L	LC50 (48h, fish) = 56 mg/L /12/
				EC50 (48h, inv.) = 0,362 mg/L	EC50 (48h, inv.) = 0,9 mg/L	EC50 (48h, inv.) = 44 mg/L /12/
				ErC50 (72h, algae) = 0,134 mg/L	ErC50 (72h, algae) = 9,317 mg/L	EC50 (96h, algae) = 200 mg/L /12/
				NOErC (72h, algae) = 0,022 mg/L	NOErC (72h, algae) = 0,952 mg/L	
					NOEC (10d, inv.) = 9,6 mg/L	NOEC (21d, inv.) = 1,3 mg/L /12/
PBT	CLP: Not T	CLP: Not T	CLP: Not T	CLP: Not T	CLP: Not T	CLP: Not T
	Conclusion: Based on the data above the substance is not a PBT substance	Conclusion: Based on the data above the substance is not a PBT substance	Conclusion: Based on the data above the sub-stance is not a PBT substance	Conclusion: Based on the data above the substance is not a PBT substance	Conclusion: Based on the data above the substance is not a PBT substance	Conclusion: Based on the data above the substance is not a PBT substance
vPvB	Conclusion: Based on the data above the substance is not a vPvB substance	Conclusion: Based on the data above the substance is not a vPvB substance	Conclusion: Based on the data above the sub-stance is not a vPvB substance	Conclusion: Based on the data above the substance is not a vPvB substance	Conclusion: Based on the data above the substance is not a vPvB substance	Conclusion: Based on the data above the substance is not a vPvB substance
Endocrine Disrupting Chemical (EDC) /4, 5, 6/	Not included /4, 5, 6/	Not included /4, 5, 6/	Not included /4, 5, 6/	Not included /4, 5, 6/	Not included /4, 5, 6/	Not included /4, 5, 6/

Substance	Ethyl Butyl Ether	Di-n-Propyl Ether	Methyl Cyclopentane	Methyl Cyclohexane	Cyclohexane	Ethyl propionate
VOC /2/ (Bp< 250 °C)	Bp = 92,3°C (1atm) /10/ (exp. data)	Bp = 90°C (1atm) /10/ (exp. data)	Bp = 72°C (1atm) /11/	Bp = 100.93°C (1atm)	Bp = 80.7°C (1atm)	Bp = 99.1°C (1atm) (exp.) /10/
	Conclusion: Volatile	**Conclusion: Volatile**	**Conclusion: Volatile**	**Conclusion: Volatile**	**Conclusion: Volatile**	**Conclusion: Volatile**
Substitute It Now (SIN list) /7/	Not included	Not included	Not included	Not included	Not included	Not included
REACH Candidate list/SVHC /8/	Not included	Not included	Not included	Not included	Not included	Not included
EU list of allergenic substances /9/	Not included	Not included	Not included	Not included	Not included	Not included

Table A-1: Substance profiles (Environment and human health evaluation). Environmental and health factors, that may cause these substances to be unsuitable alternatives for substitution, are highlighted in red. (continued)

Substance	**Ethanol**	**n-Propyl propionate**	**Isopropylformate**	**Ethylformat**
CAS	**64-17-5**	**106-36-5**	**625-55-8**	**109-94-4**
Molecular formula	C2H6O1	C6H12O2	C4H8O2	C3H6O2
Structure				
CLP /1/	**Harmonised classification:**	**Harmonised classification:**	**Not classified:**	**Harmonised classification:**
	H225 (Highly flammable liquid and vapour)	H226 (Flammable liquid and vapour)		H225 (Highly flammable liquid and vapour)
		H332 (Harmful if inhaled)		H302 (Harmful if swallowed)
				H319 (Causes serious eye irritation)
				H332 (Harmful if inhaled)
				H335 (May cause respiratory irritation)
Environmental fate /2, 3/	Biodegradation: Ready biodegradable (not P)	Ready biod. /10/	Ready biod. /10/	Inherently biodegradable
	Log Kow: -0.35	Log Kow: 1.85 /10/	Log Kow: 0.73 /10/	Log Kow: 1.504
Eco-toxicity /2,	LC50 (96h, fish) = 7,96 g/L		LC50 (96h, fish) = 63.37 mg/L	LC50 (96h, fish) >100 mg/L

Substance	Ethanol	n-Propyl propionate	Isopropylformate	Ethylformat
3/			/10/	
	EC50 (48h, inv.) = 5,012 g/L		EC50 (48h, inv.) = 153.34 mg/L /10/	EC50 (daphnia, 48h) 280 mg/L (REACH dossier, QSAR toolbox)
	ErC50 (72h, algae) = 275 mg/L		ErC50 (96h, algae) = 74.88 mg/L /10/	EC50 (algae, 72 h) 219.547 mg/L (REACH dossier, QSAR toolbox)
	ErC10 (72h, algae) = 11,5 mg/L			
PBT	CLP: Not T	CLP: Not T	CLP: Not T	CLP: Not T
	Conclusion: Based on the data above the substance is not a PBT substance	Conclusion: Based on the data above the substance is not a PBT substance	Conclusion: Based on the data above the substance is not a PBT substance	Conclusion: Based on the data above the substance is not a PBT substance
vPvB	Conclusion: Based on the data above the substance is not a vPvB substance	Conclusion: Based on the data above the substance is not a vPvB substance	Conclusion: Based on the data above the substance is not a vPvB substance	Conclusion: Based on the data above the substance is not a vPvB substance
Endocrine Disrupting Chemical (EDC) /4, 5, 6/	Not included /4, 5, 6/	Not included /4, 5, 6/	Not included /4, 5, 6/	Not included /4, 5, 6/
VOC /2/ (Bp< 250 °C)	Bp = 78.3°C (1atm)	Bp = 122.5°C (1atm) (exp.) /10/	68.2 °C (exp. value) /10/	Bp = 56.6°C (1atm)
	Conclusion: Volatile	**Conclusion: Volatile**	**Conclusion: Volatile**	**Conclusion: Volatile**
Substitute It Now (SIN list)	Not included	Not included	Not included	Not included

Substance	Ethanol	n-Propyl propionate	Isopropylformate	Ethylformat
/7/				
REACH Candidate list/SVHC /8/	Not included	Not included	Not included	Not included
EU list of allergenic substances /9/	Not included	Not included	Not included	Not included

References

/1/ ECHA CLP inventory

/2/ ECHA registration data (Search by CAS number)

/3/ Guidance on Information Requirements and Chemical Safety Assessment; Chapter R.11: PBT/vPvB assessment; Version 3.0 June 2017

/4/ Annex 13: List of 146 substances with endocrine disruption classifications prepared in the Expert meeting http://ec.europa.eu/environment/archives/docum/pdf/bkh_annex_13.pdf

/5 / G. Petersen, D. Rasmussen, K. Gustavson (2007) 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

/6/ http://ec.europa.eu/environment/chemicals/endocrine/strategy/substances_en.htm#priority_list

/7/ SIN List: http://chemsec.org/business-tool/sin-list/

/8/ SVHC: https://echa.europa.eu/da/candidate-list-table

/9/ EU list of 26 allergenic substances classified in accordance with Directive 1272/2008

/10/ Epi-suite QSAR calculation (Epi-Web 4.1) calculation based on CAS number

/11/ http://www.chemicalbook.com/CASEN_96-37-7.htm

/12/ Aquire ecotox database

Substitution of solvents in printing inks

Substitution of three solvents has been attempted: methyl ethyl ketone (MEK), toluene and extraction benzine (b. p. 100-140°C). The solvents are used to dissolve specific binders in printing inks, but are of concern due to negative effects on the human health and the environment. Alternative solvents for laboratory tests were identified using the software, Hansen Solubility Parameters in Practice ("HSPiP"). The software showed excellent correlation between theory and practice and thus saves working hours from typical trial-and-error based approaches. For three out of the four binders, the alternative solvent combinations fulfilled all technical requirements and had improved health/environment profiles. The solvent cyclopentyl methyl ether (CPME) is part of the solvent combinations for all three binders. However, at the time of writing, only a high grade of CPME is available within EU, leading to an unacceptably high price. Hence, the solutions have not yet been fully implemented and tested with Resino Inks' customers.

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