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Alternatives to MDI in Consumer Products

- with focus on coatings, adhesives and sealants

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Title:

Alternatives to MDI in Consumer Products

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Preface

Methylene diphenyl diisocyanate (MDI) is included in the Danish List of Unwanted Substances (LOUS) and has thus been subject to a survey summarising existing knowledge regarding regulation, manufacturing, uses/applications, waste handling, health, environment and alternatives. MDI was addressed in the LOUS report “Survey of certain isocyanates (MDI and TDI)” (Christensen *et al.*, 2014), hereafter the "LOUS report".

As a follow-up to the LOUS report, the current report investigates in more detail availability of alternatives to MDI in consumer products (coatings, adhesives and sealants) and assesses the health and environmental properties of these alternatives as compared to MDI.

The project was conducted by COWI A/S with support from the Danish Technological Institute from July through December 2014.

Conclusion and summary

Background and objective
Methylene diphenyl diisocyanate (MDI) was in 2009 included in the Danish List of Undesirable Substances (LOUS) as it is used in volumes above 100 tonnes/year in Denmark and as it is classified as a suspected carcinogen R40 and for danger of serious damage to health by prolonged exposure R48–according to the Dangerous Substances Directive (67/548/EEC). Of particular relevance for this project, MDI is further classified as a respiratory and dermal sensitizer.

Substances on LOUS have been subject to surveys summarising existing knowledge of the LOUS substances regarding regulation, manufacturing, uses/applications, waste handling, health, environment and alternatives. MDI was addressed in the LOUS report "Survey of certain isocyanates (MDI and TDI)", hereafter the 'LOUS report'.

The LOUS report identified a number of alternatives to MDI; some seemed to be commercially available while others were considered emerging technologies. The LOUS report concluded that the possibility of using alternatives for coating, adhesives and sealants was more promising than alternatives for the industrially produced flexible and rigid foamed PUR products. With respect to protection of consumers this is at first sight assessed as an advantage, since such consumer applications are associated with possible exposure to the monomer and thus a likelihood of presenting a consumer risk.

However, the survey also concluded that no assessment of the toxicity and risks associated with the use of some of these alternatives has been identified and that the alternatives might not be significantly better than MDI and TDI based products, as the substitutes are highly reactive chemical compounds as well.

In relation to alternatives to MDI in coatings, adhesives and sealants in consumer products and building on the preliminary findings in the LOUS project, the current project aims at:

- Identifying chemical and technical non-chemical alternatives
- Assessing human health and environmental properties of identified chemical alternatives in comparison with MDI

Identification of alternatives - survey
Scope and approach
Information has been collected through the following sources:

- The LOUS report on isocyanates (MDI and TDI)
- Contact to a number of trade organisations and companies (including visits to stores)
- Internet search
- Technical and scientific literature, patents and DIY books.

In order to identify chemical and technical non-chemical alternatives to free MDI, interviews have been carried out in two DIY centres based on an initial inspection of the products currently on the shelves. The scope was limited to identifying MDI containing coatings, adhesives and sealants as well as possible chemical and technical non-chemical alternatives considered available to consumers. In addition, further interviews with the Danish companies already consulted in the LOUS project were carried out.

The Internet search and search for technical and scientific literature, took the findings from the LOUS project as the starting point, and was further detailed in relation to consumer products.

Results - Technical non-chemical alternatives
Overall, non-chemical alternatives are scarce. The possibility for non-chemical solutions will depend on which type of material or combination of material is used in the application and whether the product is to be used for renovation or new installations.

Expanding sealant bands are deemed to be a possible replacement for sealant foams in some instances, but it is expected that the consumer in most cases will use expanding foam due to the ease of use. Other non-chemical options are to use factory made products coated or glued before distribution to consumers. Mechanical joints such as nails, spikes, screws, tongues/grooves and rivets are possible for a number of applications, but are often combined with the use of adhesives to strengthen the bonds between materials.

Most of the identified non-chemical alternatives are more applicable in relation to new installations than for repair/renovation.

Results - Chemical alternatives
Although only MDI sealant foams were recognized at the shelves in two DIY centres, a range of consumer and professional products for coatings, adhesives and sealants containing MDI or MDI alternatives were identified through the internet based search.

The survey has identified a broad range of chemical alternatives to MDI (monomers, prepolymers etc.) intended for use in coatings, adhesives and sealants (elastic and rigid foams), which to some extent are or could be available to consumers. The identified alternative substances have been arranged into six categories:

- Blocked or encapsulated MDI
- Aliphatic diisocyanates, free and blocked
- Prepolymer MDI
- Monomers for non-isocyanate-based polyurethane (NIPU)
- Monomers for hybrid non-isocyanate-based polyurethane (HNIPU)
- Monomers for other hybrid polymers based on silane chemistry

The most promising alternatives seem to be for rigid foam sealants where commercial alternatives exist. Also alternatives for other sealants and adhesives look promising.

The alternative substances (monomers) are rated based on which MDI-containing consumer products have been identified on the marked today, as well as the expected commercial availability of the alternatives based on the information gathered in this survey. The information regarding the functionality of products containing the substance, as well as the author's expert judgement has also been included in the rating. Highest priority (priority 4) is given if the alternative chemistry is considered easily available to the consumer and has been identified in consumer products on the marked or is recommended by a supplier for consumer relevant applications. Lowest priority is given if the alternative chemistry is considered an emerging technology and no specific link to use of the chemistry in products on the marked has been identified. In agreement with the Danish EPA, substances with high priority have been chosen for the health and environmental assessment of chemical alternatives. These fall within the categories: MDI-based prepolymers, monomers for hybrid non-isocyanate-based polyurethane (HNIPU) and monomers for other hybrid polymers based on silane chemistry, see below table.

MOST RELEVANT ALTERNATIVES TO MDI IN CONSUMER PRODUCTS

Trade name	Product chemistry	Application(s)	CAS no
MDI-based prepolymers			
Desmodur® E 23	Polyisocyanate prepolymer based on MDI	Adhesive (wood bonding, binder for corrosion protection), flexible packaging, metal coating	Mixture of 99784-49-3, 5873-54-1, 101-68-8
Desmoseal® M 280	Aromatic prepolymer based on MDI	Sealants, elastic adhesives	Mixture of 59675-67-1, 4083-64-1, 101-68-8
Monomers for hybrid non-isocyanate-based polyurethane (HNIPU)			
Desmoseal ® S XP 2636	Silane-terminated prepolymers (STP) - Hybrid systems of PUR with reactive silane end groups	Adhesives, sealants (low modulus with high elongation)	Mixture, not available
Desmoseal ® S XP 2458	Silane-terminated prepolymers (STP) - Hybrid systems of PUR with reactive silane end groups	Adhesives (high modulus, medium elongation)	Mixture, not available
Desmoseal ® S XP 2749	Silane-terminated prepolymers (STP) - Hybrid systems of PUR with reactive silane end groups	Adhesives (plasticizer free with high hardness)	Mixture, not available
Monomers for other hybrid polymers based on silane chemistry			
Geniosil® STP-E10 /30	Dimethoxy(methyl) silylmethyl-carbamate-terminated polyether (alpha-silane)	Adhesives, sealants (and coatings)	611222-18-5
Geniosil® STP-E15/35	Trimethoxysilylpropylcarbamate-terminated polyether	Adhesives, sealants and coatings	216597-12-5
Geniosil® XB502	silane-terminated binder based on alpha-silane technology (alpha-silane)	Adhesives, sealants and coatings	Not available
Geniosil® GF 9 / SiSiB® PC1200	N-(2-Aminoethyl)-3-aminopropyltrimethoxysilane (Amino functionalised silane)	Adhesives, sealants and coatings	1760-24-3
Geniosil® GF 93 / SiSiB® PC1100	3-Aminopropyl-triethoxysilane (Amino functionalised silane)	Adhesives, sealants and coatings	919-30-2
Geniosil® GF 95	N-(2-Aminoethyl)-3-aminopropylmethyldimethoxysilane (Amino functionalised silane)	Adhesives, sealants and coatings	3069-29-2
Geniosil® GF 96	3-Aminopropyl-trimethoxysilane (Amino functionalised silane)	Adhesives, sealants and coatings	13822-56-5
Geniosil® GF 98	3-Ureidopropyl-trimethoxysilane (Amino functionalised silane)	Adhesives, sealants and coatings	23843-64-3
Geniosil® GF 80	3-Glycidoxypropyl-trimethoxysilane (Epoxy functionalised silane)	Adhesives, sealants and coatings	2530-83-8
Geniosil ® XL 10	Vinyltrimethoxysilane	Adhesives, sealants and coatings	2768-02-7

Assessment of health and environmental issues

Scope and approach

The assessment of health and environmental properties focuses on the "priority 4" chemical alternatives identified in the market survey.

The alternatives are initially divided and assessed in four groups:

- Prepolymer MDI (2 alternatives)

- Monomers for HNIPU (3 alternatives)
- Monomers for other hybrid polymers based on silane chemistry (main monomers) (3 alternatives)
- Monomers for other hybrid polymers based on silane chemistry (adhesion promoters) (7 alternatives)

The two latter are used together and the comparative assessment with MDI-based products thus takes main monomers as well as adhesion promoters into account.

For each group, the inherent properties of the identified alternatives are compared with MDI based on their classification and physico-chemical properties, and where needed further hazard data (toxicity, environmental fate and ecotoxicity) have been collected with main focus on hazards, exposure and risks for consumers.

Actual risks of the alternatives not only depend on the inherent properties of alternatives to MDI, but also on exposure, including how the alternative is applied and in which amounts. Further, the other components/co-formulants of an adhesive, coating and sealant product are crucial for the overall hazard and risk. It has been beyond the scope of the current study to assess risks in detail, but some considerations based on the available information are provided.

Main information sources for assessing the alternatives have been: i) suppliers Safety Data Sheets, ii) OECD Screening Information Data Set (SIDS), iii) information on ECHA's web-site (classification and labelling inventory and dissemination portal for substances registered under REACH).

Results
Within the scope of this project, the following can be concluded for these types of alternatives:

Prepolymer MDIs seem to inherently possess the same toxicity as 'pure'/'free' MDI and the available information on use and exposure potential does not indicate any significantly reduced risks from using these alternatives.

The **HNIPU monomers** are assessed to potentially lead to significant reduction in consumer hazards and risks.

It should however be stressed that this assessment is based on:
- Limited knowledge about the composition of the HNIPU monomers (claimed to contain 'no dangerous substances' in the supplier Safety Data Sheets) and consequently, the assessment is based solely on information in the supplier Safety Data Sheets
- Limited knowledge about which co-formulants, including possible organic solvents, would be needed in addition to the HNIPU monomers for formulating adhesives, coatings and sealants.

Systems based on **monomers for 'other hybrid silane'** chemistry would typically contain: i) a 'main monomer' and ii) an 'adhesion promotor' and/or a water scavenger, in addition to other co-formulants.

All in all, these systems seem to possess lower severe inherent toxicity (carcinogenicity and sensibilisation), but would introduce other exposure/risk factors, including potential for releasing methanol (which might cause severe systemic toxicity following dermal contact or following evaporation via inhalation) and a higher potential for irritation of/effects on eye and skin (classified for eye damage and skin corrosion).

To this end, it should be noted that MDI is subject to an EU restriction requiring that gloves and extended safety information is supplied along with MDI-based products to consumers. This is not the case for 'other hybrid silane' chemistry alternatives.

In addition, phthalates might be used as plasticizers in 'other hybrid silane'-based products.

None of these alternatives are considered to possess environmental fate and hazard properties significantly different than those of MDI.

Thus, in relation to possibly substituting MDI, alternative products would have to be assessed case-by-case, considering:

- The degree to which methanol could be released in a given exposure scenario
- The concentration of 'other hybrid silane' monomers (affecting the potential for eye damage and skin corrosion)
- Other co-formulants (including e.g. plasticizers, where 'example formulations' in technical data sheets for 'other hybrid systems' mention phthalates as an option).

Further survey and/or experimental activities on these issues would be needed to possibly being able to draw firm conclusions on MDI-based products versus products based on 'other hybrid silane' chemistry.

Thus, based on the current study, no overall conclusion can be reached for 'other hybrid silane' systems as alternatives to MDI-based systems.

Conclusion

The following table summarises the pros and cons for the identified alternatives as compared to MDI in consumer products, based on the knowledge identified and assessed in the current project:

Type of alternative	Pros	Cons
Prepolymer MDIs	None identified	Similar hazard as MDI monomers and possibly similar risk
HNIPU monomers	Based on suppliers Safety Data Sheets: - Less hazardous - Possibly lower consumer risk	Limited information available on: - Composition - Possibly toxic co-formulants in final products
Monomers based on 'Other hybrid silane' chemistry	- Less hazardous in terms of sensitization and carcinogenicity	- Release methanol during use/applications -> depending on amount this could cause consumer inhalation and dermal exposure and possible risks - Monomers are more hazardous in terms of irritation/corrosion potential (including classification for eye damage) - Care should be taken in relation to co-formulants. The suppliers e.g. suggest that phthalates could be used as plasticizers, and various organic solvents might be used in foam sealants

Konklusion og sammenfatning

Baggrund og formål
Methylendiphenyldiisocyanat (MDI) blev i 2009 optaget på listen over uønskede stoffer (LOUS), da det anvendes i mængder over 100 tons/år i Danmark, og da det er klassificeret som mistænkt for at være kræftfremkaldende (R40) og med fare for alvorlig sundhedsfare ved længere tids påvirkning (R48) i henhold til direktivet om farlige stoffer (67/548/EØF). Af særlig relevans for dette projekt er, at MDI yderligere er klassificeret som sensibiliserende ved indånding og hudkontakt.

Stoffer optaget på LOUS har været genstand for kortlægninger, som sammenfatter den eksisterende viden om LOUS stofferne med hensyn til regulering, produktion, anvendelser, affaldshåndtering, sundhed, miljø og alternativer. MDI blev behandlet i LOUS-rapporten "Survey of certain isocyanates (MDI and TDI)", herefter kaldet "LOUS-rapporten".

LOUS-rapporten identificerede en række alternativer til MDI, hvoraf nogle blev anset for kommercielt tilgængelige, mens andre ansås at være teknologier under udvikling. LOUS-rapporten konkluderede, at muligheden for at anvende alternativer til overfladebehandlingsmidler, lime/klæbestoffer og fugemasser virkede mere lovende end alternativer til industriel produktion af fleksible og stive PUR-produkter. Med tanke på beskyttelse af forbrugerne er dette umiddelbart vurderet en fordel, da netop sådanne forbrugeranvendelser er forbundet med mulig udsættelse for monomeren og dermed en mulig forbrugerrisiko.

LOUS-projektet identificerede imidlertid ikke undersøgelser/vurderinger af toksicitet og risici forbundet med anvendelsen af disse alternativer og konkluderede, at alternativerne muligvis ikke er væsentligt bedre end de reaktive MDI- og TDI-baserede produkter, da alternativerne også må besidde reaktive egenskaber.

Med udgangspunkt i de foreløbige resultater fra LOUS-rapporten, har dette projekt nærmere undersøgt alternativer til MDI i overfladebehandlingsmidler, lime/klæbestoffer og fugemasser i forbrugerprodukter. Projektet har til formål at:

- Identificere kemiske og tekniske ikke-kemiske alternativer
- Vurdere sundheds- og miljømæssige egenskaber af de identificerede kemiske alternativer sammenlignet med MDI

Alternativer - kortlægning
Afgrænsning og metode

Information er indsamlet fra følgende kilder:
- LOUS-rapporten om isocyanater (MDI og TDI)
- En række brancheorganisationer og virksomheder (herunder butiksbesøg)
- Søgning på internettet
- Teknisk og videnskabelig litteratur, patenter og "gør-det-selv"-bøger

For at identificere kemiske og tekniske ikke-kemiske alternativer til MDI, blev der gennemført interview i to byggemarkeder, baseret på en indledende inspektion af nuværende produkter på hylderne. Inspektionen/interviewet var afgrænset til at identificere MDI-baserede overfladebehandlingsmidler (herunder f.eks. maling), lime/klæbestoffer og fugemasser, samt eventuelle kemiske og tekniske ikke-kemiske alternativer tilgængelige for forbrugerne. Derudover blev der gennemført mere detaljerede interviews med de danske virksomheder, som allerede havde bidraget i forbindelse med LOUS-rapporten.

Internet-søgningen og søgningen efter teknisk og videnskabelig litteratur tog udgangspunkt i resultaterne fra LOUS-rapporten. Søgningerne blev specifikt målrettet de forbrugerprodukter, som projektet omhandler.

Resultater - Tekniske ikke-kemiske alternativer
Overordnet set er der få tilgængelige ikke-kemiske alternativer. Muligheden for at anvende ikke-kemiske alternativer vil afhænge af, hvilken type materiale eller kombination af materialer som anvendes og om produktet skal anvendes til reparation/renovering eller nye installationer.

Ekspanderende fugebånd vurderes at være en mulig erstatning for fugeskum, men det forventes, at forbrugeren i de fleste tilfælde vil vælge det mere brugervenlige fugeskum. Andre ikke-kemiske muligheder er at anvende fabriksfremstillede produkter, som er overfladebehandlet eller limet inden distribution til forbrugerne. Mekaniske løsninger, såsom søm, nagler, skruer, spænder, noter og nitter er relevante for en række anvendelser, men er ofte kombineret med anvendelse af lime/klæbemidler til at styrke sammenføjningen af materialerne.

De fleste af de identificerede ikke-kemiske alternativer er mere anvendelige i relation til nye installationer end til reparation/renovering.

Resultater - kemiske alternativer
Selv om der kun blev identificeret MDI fugeskum på hylderne i de to inspicerede byggemarkeder, blev der via internet-søgning identificeret en række overfladebehandlingsmidler, lime/klæbestoffer og fugemasser til forbrugere og professionelle, dels baseret på MDI og dels baseret på alternativer til MDI.

Kortlægningen identificerede en lang række kemiske alternativer til MDI (monomerer, præpolymerer etc.) beregnet til anvendelse i overfladebehandlingsmidler, lime/klæbestoffer og fugemasser/fugeskum, som til en vis grad er eller kan være til rådighed for forbrugerne. De identificerede alternativer er blevet inddelt i seks kategorier:

- Blokeret eller indkapslet MDI
- Alifatiske diisocyanater, frie og blokerede
- MDI præpolymere
- Monomere til ikke-isocyanat-baseret polyuretan (NIPU: Non-isocyanate-based polyurethane)
- Monomere til hybrid ikke-isocyanat-baseret polyuretan (HNIPU: Hybrid non-isocyanate-based polyurethane)
- Monomere til andre hybridpolymere baseret på silan-kemi

Den mest lovende substitutionsmulighed synes at være for fugeskum, hvor der findes kommercielle alternativer. Også alternativer til anvendelse i fugemasser og lime ser lovende ud.

De alternative stoffer (monomere) er blevet prioriteret ud fra, hvor MDI-holdige forbrugerprodukter er blevet identificeret på markedet i dag, samt den forventede kommercielle tilgængelighed af alternativerne baseret på de oplysninger, der er indsamlet i denne kortlægning. Oplysningerne om funktionaliteten af produkter, der indeholder stoffet, samt forfatterens ekspertvurderinger er også blevet inkluderet i denne prioritering. Højeste prioritet (prioritet 4) er givet, hvis den alternative kemi anses for lettilgængelig for forbrugeren og er blevet identificeret i forbrugerprodukter på markedet eller anbefales af en leverandør til relevante forbrugeranvendelser. Laveste prioritet er givet, hvis den alternative kemi betragtes som en ny/kommende teknologi, og der ikke er identificeret konkret anvendelse af denne kemi på markedet. Efter aftale med den danske Miljøstyrelse, blev stoffer med højest prioritet udvalgt til sundheds- og miljømæssig vurdering. Disse alternativer falder ind under kategorierne: MDI præpolymere, monomere til hybrid ikke-isocyanat-baseret polyuretan (HNIPU) og monomere til andre hybridpolymere baseret på silan-kemi, se tabellen i den engelske sammenfatning.

Sundheds- og miljøvurdering

Afgrænsning og metode

Vurderingen af sundheds- og miljømæssige egenskaber fokuserer på de højest prioriterede stoffer (prioritet 4) fra kortlægningen.

Alternativerne er opdelt og vurderet i fire grupper:
- MDI præpolymere (2 alternativer)
- Monomere til HNIPU (3 alternativer)
- Monomere til andre hybridpolymere baseret på silan-kemi (hovedmonomer) (3 alternativer)
- Monomere til andre hybridpolymere baseret på silan-kemi (adhæsionsfremmer) (7 alternativer)

De to sidstnævnte anvendes sammen og den sammenlignende vurdering med MDI-baserede produkter tager således hensyn til såvel hovedmonomer som adhæsionsfremmer.

For hver af disse grupper er de iboende egenskaber af alternativerne sammenlignet med MDI, baseret på deres klassificering og fysisk-kemiske egenskaber, og hvor der er behov for yderligere faredata (toksicitet, skæbne i miljøet og økotoksicitet) er data indsamlet med fokus på fare, eksponering og risiko for forbrugeren.

Den reelle risiko forbundet med alternativerne er dog ikke alene afhængig af de iboende egenskaber af alternativerne sammenlignet med MDI, men også af eksponering, herunder hvordan alternativet anvendes, og i hvilke mængder. Endvidere er de andre komponenter/hjælpestoffer af overfladebehandlingsmidler, lime/klæbestoffor og fugemasser afgørende for den samlede potentielle fare og risiko. Det har været uden for rammerne af dette studie at vurdere risici i detaljer, men rapporten giver nogle overvejelser baseret på de foreliggende oplysninger.

De væsentligste informationskilder til vurderingen af alternativerne har været: i) sikkerhedsdatablade fra leverandørerne, ii) Stof Informations Datablade fra OECD (SIDS: Screening Information Data Set), iii) oplysninger på Kemikalieagenturets (ECHAs) hjemmeside (klassificering og mærkning og formidlingsportalen (dissemination portal) for stoffer registreret under REACH).

Resultater

Inden for rammerne af dette projekt, kan følgende konkluderes for disse typer af alternativer:

MDI præpolymere ser ud til at besidde den samme iboende toksicitet som frie MDI monomere og den tilgængelige information om anvendelse og eksponeringspotentiale indikerer ikke nogen signifikant reduceret risiko ved at anvende disse alternativer.

HNIPU monomere vurderes potentielt at kunne lede til betydelig reduktion i fare og risiko for forbrugerne.

Det skal dog understreges, at denne vurdering er baseret på:
- Begrænset viden om sammensætningen af HNIPU monomerene (deklareret til at indeholde "ingen farlige stoffer" i leverandørens sikkerhedsdatablad) og dermed er vurderingen udelukkende baseret på oplysninger i disse sikkerhedsdatablade.

- Begrænset viden om, hvilke komponenter/hjælpestoffer udover HNIPU monomere, herunder eventuelle organiske opløsningsmidler, der ville være behov for i overfladebehandlingsmidler, lime/klæbestoffer og fugemasser.

Systemer baseret på **monomere af "anden hybrid silan-kemi"** vil typisk indeholde: i) en "hovedmonomer" og ii) en "adhæsionsfremmer" og/eller et vanddrivningsmiddel, foruden andre hjælpestoffer.

Alt i alt synes disse systemer til at besidde mindre alvorlig iboende toksicitet (carcinogenicitet og overfølsomhed), men ville medføre andre eksponerings-/risikofaktorer, herunder mulighed for at frigive methanol (der kan forårsage alvorlig systemisk toksicitet efter hudkontakt eller via inhalation efter fordampning) og et højere potentiale for irritation af/effekter på øjne og hud (klassificeret som øjenskadende og ætsende).

I den sammenhæng skal det bemærkes, at MDI er omfattet af en EU anvendelsesbegrænsning, der kræver, at handsker og udvidede sikkerhedsoplysninger leveres sammen med MDI-baserede produkter til forbrugere. Dette er ikke tilfældet for alternativer baseret på "anden hybrid silan-kemi".

Desuden kan produkter baseret på "anden hybrid silan-kemi" indeholde ftalater som blødgørere.

Ingen af disse alternativer vurderes at besidde miljømæssige egenskaber, som er væsentligt anderledes end MDI.

I forbindelse med eventuel substitution af MDI, skal alternative produkter med "anden hybrid silan-kemi" således vurderes fra sag til sag og tage hensyn til:
- I hvor høj grad methanol kan frigives i et givet eksponeringsscenarie.
- Koncentrationen af "anden hybrid silan-kemi" monomere (påvirker potentialet for øjenskader og hudætsning).
- Andre komponenter/hjælpestoffer (herunder eksempelvis blødgørere, hvor "eksempelformuleringer" i de tekniske datablade for monomere baseret på "anden hybrid silan-kemi" nævner ftalater, som en mulighed).

Yderligere undersøgelser og/eller eksperimentelle aktiviteter vedr. ovenstående ville være nødvendige for at kunne drage mere præcise konklusioner vedr. sammenligning af MDI-baserede produkter og produkter baseret på "anden hybrid silan-kemi".

Baseret på dette studie kan der således ikke drages nogen overordnet konklusion vedr. "anden hybrid silan-kemi", som alternativ til MDI-baserede systemer.

Konklusion
Den følgende tabel opsummerer fordele og ulemper ved de identificerede alternativer sammenlignet med MDI i forbrugerprodukter baseret på den viden, som er identificeret og vurderet i nærværende projekt:

Alternative - type	Fordele	Ulemper
MDI præpolymere	Ingen identificerede	Samme type fare som MDI monomere og sandsynligvis tilsvarende risiko
HNIPU monomere	Baseret på leverandørernes sikkerhedsdatablade: - Mindre farligt - Muligvis mindre risici for forbrugerne	Begrænset tilgængelig information vedr.: - Sammensætning - Mulige toksiske komponenter/hjælpestoffer i færdige produkter

Alternative - type	Fordele	Ulemper
Monomere baseret på "anden hybrid silan-kemi"	- Mindre toksiske i forhold til kræftfremkaldende og sensibiliserende egenskaber	- Frigiver methanol i forbindelse med brug -> afhængig af mængden kunne dette lede til indånding og hudkontakt og mulig risiko forbrugeren - Monomere er mere toksiske end MDI i forhold til potentiale for irritation/ætsning (herunder klassifikation for øjenskader) - Der skal udvises forsigtighed i relation til andre komponenter/hjælpestoffer i de færdige produkter. Leverandørerne foreslår f.eks., at der kan anvendes ftalater som blødgører og der anvendes en række organiske opløsningsmidler i fugeskum

1. Introduction

1.1 Background

Methylene diphenyl diisocyanate (MDI) was in 2009 included in the Danish List of Unwanted Substances (LOUS) (Danish EPA, 2011). The reason for inclusion was that the substance is used in volumes above 100 tonnes/year in Denmark and that it is classified as a suspected carcinogen (R40) and for danger of serious damage to health by prolonged exposure (R48) – according to the Dangerous Substances Directive (67/548/EEC). Of particular relevance for this project, MDI is further classified as a respiratory and dermal sensitizer.

Substances in LOUS have been subject to surveys summarising existing knowledge of the LOUS substances regarding regulation, manufacturing, uses/applications, waste handling, health, environment and alternatives. MDI was addressed in the LOUS report "Survey of certain isocyanates (MDI and TDI)", hereafter the "LOUS report" (Christensen *et al.*, 2014).

The LOUS report outlines that MDI exists as different isomers (2.2'-MDI, 2,4'-MDI, 4,4'-MDI) and as mixtures of these isomers. Further, MDI is often supplied as so-called modified or prepolymer MDI. The LOUS report outlines that all these forms of MDI are generally considered (also by industry) to possess similar hazards and should therefore be classified in the same way. Consequently, these forms will generally be referred to as MDI in this report.

One exception will be that some prepolymers identified as relevant in this project are marketed as less hazardous than MDI as such. This will be discussed in more detail during the project.

Further details on types and terminology can be found in the LOUS-report, also outlining that quite some confusion exists in relation to terminology.

Based on a literature search and interviews with a selected number of companies and trade associations, the LOUS report identified a number of alternatives to MDI, some looked commercially available while others were considered emerging technologies. The LOUS report concluded that the possibility of using alternatives for both TDI and MDI for coating, adhesives and sealants looked more promising than using alternatives for the industrially produced flexible and rigid foamed PUR products (Christensen *et al.*, 2014). This was considered fortunate with respect to protection of consumers against exposure to free aromatic diisocyanates (such as MDI), since such consumer applications are associated with possible exposure and thus a likelihood of presenting a consumer risk.

However, the survey also concluded that no assessment of the toxicity and risks associated with the use of some of these alternatives had been identified and that the alternatives might not be significantly better than MDI and TDI based products, as the substitutes are highly reactive chemical compounds as well.

Building on the preliminary findings in the LOUS project, the current project will further detail the mapping, as well as health and environmental assessment of alternatives to MDI in coatings, adhesives and sealants as used by consumers.

The results from the LOUS report serves as background information and starting point for the mapping of alternatives to MDI in this project. Thus, the mapping from the earlier LOUS project has been updated with knowledge and further information identified in a search within the scope of this project. The current report can be read as a stand-alone report, as the relevant information from the LOUS project is included in this report as well.

1.2 Objective

Focusing on alternatives to MDI in coatings, adhesives and sealants in consumer products, the project aims at:

- identifying chemical and technical non-chemical alternatives
- assessing human health and environmental properties of identified chemical alternatives in comparison with MDI

2. Mapping of alternatives to MDI in consumer products

2.1 Approach

Information has been collected through the following sources:

- The LOUS project on isocyanates (MDI and TDI) (Christensen *et al.*, 2014)
- Renewed contact to a number of actors already contacted in the LOUS project:
    - ISOPA (European Diisocyanate & Polyol Producers Association)
    - Danish Coatings and Adhesives Association (DFL)
    - CEPE (European Council of the Paint, Printing Ink and Artists' Colorants)
    - FEICA (Association of the European Adhesive & Sealant Industry)
- Contact to selected companies
- Internet search
- Technical and scientific literature, patents and DIY books

Interviews have been carried out in two DIY centres based on an initial inspection of the products currently on the shelves. The aim was to identify MDI containing coatings, adhesives and sealants as well as possible chemical and technical non-chemical alternatives to MDI-based coatings, adhesives and sealants. In addition, further interviews with the Danish companies already consulted in the LOUS project were carried out.

Easily accessible literature on DIY-work has been identified and reviewed (Boile, 2007; Cassell and Parham, 2007; Træinformation, 2010; Vasegaard, 1999). The results from the interviews and the literature search are evaluated taking into account the authors' expert knowledge on the chemistry of materials and products and consultation of colleagues with expertise in building technology. Focus has been on alternatives that are commercially available for consumers.

An extended search on chemical alternatives within the more narrow scope of this project (coatings, adhesives and sealants for consumer use) has been performed in order to gain more detailed and specific knowledge on the application of MDI alternatives in such products.

The Internet search included the key words used in the earlier LOUS project: Non-isocyanate polyurethane (NIPU), Hybrid non-isocyanate polyurethane (HNIPU), blocked isocyanates, encapsulated isocyanates, alternatives to MDI, alpha-silanes, coatings, adhesives, sealants, alone or in combination. Search in the combination with toxicity and chemistry and the above terms were performed. The search has preferably been conducted using English terms, but Danish terms have also been used to identify commercially available products on the Danish marked.

Alternative isocyanates to MDI like aliphatic isocyanates have been included in the mapping because the initial literature search suggested that aliphatic isocyanates can be used as an alternative for coatings, which do not get yellow by weathering like the MDI-based coatings typically do.

2.2 Overview of the findings pertaining to alternatives in the LOUS project: "Survey of certain isocyanates (MDI and TDI)"

The information and conclusions in the LOUS project (Christensen *et al.*, 2014) are summarised in the following with focus on the scope of the current project addressing coatings, adhesives and sealants in consumer products.

A mini survey was carried out with the aim of identifying MDI and TDI containing coatings, adhesives and sealants and possibly alternatives on the Danish market through contact to producers and retailers. For several of the interviewed companies there were no suggested alternatives to MDI/TDI based products, but some alternatives were identified.

The products identified in the survey included paint for cement, paint for concrete floor, hardener for two-component PUR coating, protective coats for civil infrastructure, protective paints for on- and offshore applications, foam sealants and wood adhesive. These product types are for the main part not considered relevant in a survey targeted consumer products, but the survey showed that some products containing MDI and TDI are available to consumers. The companies were asked about alternatives to MDI/TDI based products and associated pros and cons.

The report also contains results on a survey on alternatives to MDI and TDI based on available literature. Identified alternatives in the report include:

- Prepolymers of isocyanates:
  Monomeric or polymeric MDI which has partly reacted with di- or polyfunctional alcohols. These are alternatives in applications such as wood coatings, corrosion protection, floor coatings, elastic adhesives in transportation, parquet adhesives, engineered wood constructions, flexible film lamination and sealants
- Blocking of the isocyanate groups:
  Modification of the isocyanates by blocking with other chemical agents which are loosely bound to the isocyanate and released when needed
- Alternative isocyanates:
  Commercial isocyanates other than MDI and TDI available on the marked, e.g. aliphatic isocyanates, mostly for special purpose urethane applications.
- Monomers for Non-isocyanate based PUR (NIPU):
  PUR produced without the use of isocyanates. The alternative route is based on the reaction between cyclic carbonates and aliphatic and cycloaliphatic amines.
- Other alternative monomers to produce materials:
  Use of other monomers for producing alterative materials such as polystyrene, polyolefins, epoxy, silicone and latex foams. Also newer materials such as those based on silane chemistry.

The conclusion on alternatives in the LOUS report was that possible alternatives to MDI can be identified and seem to be commercially available at least to some extent. A number of emerging technologies were identified as well. However, the detailed knowledge of application in the industry and by consumers as well as of the exposures, hazards and risks associated with alternatives compared to MDI is low. Assessments comparing health and safety aspects of alternatives with those based on isocyanate chemistry in a systematic way could not be identified, but e.g. US EPA in their recent MDI and TDI action plans note that environmentally friendly substitution seems difficult (US EPA, 2011). They also note that consumers might have or get access to MDI-based products intended for professionals.

2.3 Applications in coatings, adhesives and sealants

This survey will include technical non-chemical as well as chemical alternatives to MDI for the consumer products coatings, adhesives and sealants. Non-chemical alternatives are in this project defined to include prefabricated Do-It-Yourself (DIY) products such as already coated components (already cured rubber); thermoplastic elastomers based profiles (where the choice of material eliminates the use of MDI) and physical joints and bands.

2.3.1 Coatings

In this survey, wood coatings have been the primary focus when searching for MDI alternatives, since applications in this area was identified as the most probable (Boile, 2007; Christensen *et al.*, 2014). Uses include coatings for floors, indoor wood, furniture and outdoor wood (Boile, 2007). Use of PUR based coatings for kitchen work tops made from soft wood (pine) is also an application mentioned.

However, coatings for concrete floors are also a possible DIY application. Many applications for PUR coatings are industrial e.g. for corrosion protection in the transport industry (cars). Two component PUR coatings are primarily used for floors with high wear and tear e.g. applied in sports centres typically by professionals and not by the consumers.

For concrete paint based on prepolymeric MDI, epoxy was suggested as an alternative in the earlier LOUS report, but it was questioned whether epoxy would be less toxic. The epoxy solutions would likely have better adhesion and chemical resistance properties, but a drawback would be that the user has to handle a 2-pack system (need for mixing and stirring) (Christensen *et al.*, 2014).

2.3.2 Adhesives

PUR based adhesives can be used for some wood applications instead of the most commonly used adhesives based on polyvinyl acetate. The PUR based adhesive hardens in the presence of humidity. The PUR adhesive can join wood to wood (like the polyvinyl acetate adhesives) as well as wood to metal, concrete and hard plastics making the PUR based adhesives more universal in its application.

For wood adhesives, silyl-modified polyether (so called MS-polymer) and silyl-modified polymer (so called SMP) based products were indicated as possible alternatives in the earlier LOUS report. For wood adhesive, it was pointed out that these solutions will be 3-4 times more expensive and that tradition is a barrier for substitution (Christensen *et al.*, 2014).

2.3.3 Sealants

Sealants can be divided in plastic-, elastic- and rigid types. The plastic types are typically the acrylic based and have a rather low elasticity, which limits their use. The plastic types do not include PUR based materials and is for this reason not treated any further in this survey.

Elastic sealant types

Elasticity is an important property for sealants for some applications because different materials do not have the same thermal expansion coefficient, which means that it is necessary to assure a certain flexibility of the sealant when different materials are joined. Elastic sealants are used for applications such as gaps between windows and doors (both indoor and out-door), gaps between floor tiles and walls, behind floor panels, around pipes as well as some DIY work on cars, campers and boats (Boile, 2007).

The elastic types are typically PUR- or silicone based. They both have high elasticity and have good ageing resistance. The PUR types have to be protected against UV light e.g. by painting or addition of UV stabilizers in order not to change colour and properties. They have a good tack against most materials and a good elasticity (10 -25 %), but a primer might be necessary on porous surfaces. The silicone types have a very high elasticity (25 – 60 %) and a good tack against all materials. They can however not be painted like the PUR types. It is our impression that the silicone based products are preferred over the PUR products by the consumer based on a larger availability of silicone based products in e.g. DIY centres.

For joint sealants, MS-polymers and SMP based alternatives were found in the earlier LOUS project but these are considered more expensive and barriers for substitution are lower chemical resistance as well as consumer tradition (Christensen *et al.*, 2014).

Rigid sealant types

The rigid sealants (rigid foams) have both sealing and isolating properties at the same time. They are usually based on PUR chemistry and is used for big cracks and holes, e.g. around windows or pipes. Contrary to the elastic sealants, the rigid foams do not have elasticity, but do have good tack properties to all materials (Boile, 2007).

Foam sealants based on silane/silane terminated polymer solutions were suggested as alternatives to isocyanate based products in the earlier LOUS project. Silane/silane terminated polymers based products (called e.g. STP) however do not according to the answers from the mini survey have the same "fill effect" and would thus be about 8-9 times more expensive per volume filled. Rockwool based on mineral wool glued with a phenolic resin, was also suggested as an alternative for foam sealants (a non-chemical alternative). Rockwool would be cheaper, but would also not have the same fill-effect as MDI-based sealants (Christensen *et al.*, 2014).

2.4 Focus on applications and alternatives in this survey

Alternatives to foamed MDI-based sealants for indoor and outdoor sealing of e.g. windows and around pipes seem to exist commercially based on chemistry such as HNIPU and other hybrid materials. The focus in this survey there has primarily been on this application.

Alternatives to the PUR based elastic sealants will also be covered and as for the foamed sealants, HNIPU based alternatives also exist in this case and are easily available to the consumer.

Coatings and adhesives will to a lesser extend be covered in this survey, because the assessment is, that in most cases the applications will be for professionals and for the industrial sector. For this reason it is foreseen that only in limited cases the consumer will be exposed to MDI by using coatings and adhesives.

Regarding the chemistry of the alternatives, it has been very difficult to obtain exact information on the formulations used in commercial products. For this reason the proposed chemical substances prioritised for the health and environmental survey is mainly based on expert evaluation carried out by experts in polymer chemistry based on the available information gained during the survey combined with pre-existing knowledge about these applications and sectors.

One has to have in mind the complexity of these types of formulations. They will not only contain the reactive substances such as the isocyanates, but also a wide range of additives like UV-stabilizers, inorganic filler, plasticizers (e.g. phthalates) and catalysts (e.g. organo-tin substances or tertiary amines). These substances will also contribute to the health and environmental impact of the product. For commercial products available for the consumers, the exact formulary is unknown and confidential and only some chemical substances need to be declared on the Safety Data Sheet. In any case, the focus of this survey has been on alternative monomers to MDI.

Another issue with respect to the survey on chemical alternatives is that the suppliers of raw materials and manufacturers of the final products use different nomenclature for similar or identic chemistry due to patent rights, trademark protection and marketing.

2.5 Results - Product search on available MDI products and alternatives

Through the internet search conducted, a number of products containing MDI or alternatives to MDI have been found within each of the applications coatings, adhesives and sealants, as described above. A few products have also been identified during visits to two DIY centres.

For coatings, a few products for coating of wood and concrete floors as well as some products for metal coating can be found and some are available through internet stores. Products containing MDI as well as products claimed to be isocyanate free have been identified. For most products claiming to be "isocyanate free", very little information is available regarding the alternative chemistry used in the products. According to technical information sheets found, some coatings are e.g. acrylic (Lactam, 2009; PPG, 2008; HiChem Industries, 2000) while others are claimed to be based on so called “Green Polyurethane” (NTI, 2014). No coating products based on MDI chemistry were found on the shelves at the two DIY centres.

For adhesives, a few products for joining materials such as metal, plastics wood, aluminium, composites and concrete can be found and some are available through internet stores. Products containing MDI as well as products claimed to be isocyanate free have been identified. For most products claiming to be isocyanate free, some information is available regarding the alternative chemistry used in the products. Identified adhesives which claim to be isocyanate free are, according to technical datasheets from the manufacturer/distributor, based on hybrid materials such as MS-polymer (Permabond, not dated), SMX (Soudal, 2008) or STP (Weiss Chemie, 2011). No adhesives based on MDI chemistry were found on the shelves at the two DIY centres.

For sealants, the products identified fall into two categories; elastic sealants and rigid foams. There are a larger number of products with alternatives to MDI within these categories as compared to adhesives and coatings.

Rigid foam products containing MDI as well as products claimed to be isocyanate free have been identified. For most products claiming to be isocyanate free, some information is available regarding the alternative chemistry used in the products. Foams found which are claimed to be isocyanate free are, according to technical datasheets from the manufacturer/distributor, based on hybrid materials such as SMX (Soudal, 2006) or STP (Dana Lim, 2013). At the two DIY centres all rigid foams found on the selves were based on MDI chemistry.

Elastic sealants containing isocyanate as well as products claimed to be isocyanate free have been identified. For most products claiming to be isocyanate free, some information is available regarding the alternative chemistry used in the products. The identified sealants, which are claimed to be isocyanate free, are according to technical datasheets from the manufacturer/distributor, based on hybrid materials such as SiMP based (Headway Chemicals, 2011) or MS-polymer based (Ljungdahl, not dated; Dana Lim, 2012). Others only claim that the products are based on hybrid materials (BASF, not dated; workshopping.co.uk, not dated). No elastic sealants based on MDI chemistry were found on the shelves at the two DIY centres

2.6 Results - Non-chemical alternatives

An overview of relevant suggestions for non-chemical alternatives to MDI-based products is given in Table 1. In the DIY literature consulted (Boile, 2007; Cassell and Parham, 2007; Træinformation, 2010; Vasegaard 1999), the substitution of chemical solutions with non-chemical solutions is not a topic typically addressed explicitly. However, one can find many technical hints and recommendations for DIY solutions without the use of reactive chemicals.

Coatings

For some applications, factory treated products and semi-finished products are available, e.g. floors and panels with an already coated surface which eliminate the consumer exposure to uncured coatings altogether. Thus floor boards are available which are made of polyolefins with a coat of PUR or another abrasive resistant coat. Another possibility is floor boards with a cork core and with an abrasive resistant coat. Most of these alternatives are applicable in new installations/treatments, whereas for renovations of existing surfaces (e.g. treatment of existing floors due to wear), the option of replacing the entire surface with pre-treated materials are associated with a large workload and not considered economical viable. Thus, for consumers renovating installations e.g. in their homes, no realistic non-chemical alternatives are found.

Adhesives

In both DIY centres, very few non-chemical alternatives were identified for gluing together wood or other materials other than physical joints. Physical joints could be an alternative for some applications. Physical joints include bolting, screwing, nails used to join prefabricated profiles of e.g. wood together with another material. Physical joining of materials is not always a possibility, e.g. it does not always provide the sealing effect or required strength of an adhesive, or is not physically possible due to dimensional restraints. The visual appearance can also limit the applicability.

Some materials can be joined by welding the materials together using heat, e.g. fusing two pieces of plastic or even metal and glass. Welding typically requires high temperatures and is not considered a realistic non-chemical alternative in the consumer context of this survey.

As for coatings, most of the alternatives for adhesives are considered more applicable in new installations, whereas for renovations of existing joints, the option of choosing a non-chemical alternative are considered more difficult and will probably be associated with a larger workload, if even possible. Thus, for consumers renovating installations e.g. in their homes, no realistic non-chemical alternatives are found.

Sealants

According to Vasegaard (1999), an ideal sealing of a window frame in a brick house with wood windows is to fill the gap between the window and wall with mineral wool and seal with lime mortar. However, it is assumed that the consumers in most cases will choose the sealants foams because they are very easy to use even for a non-professional.

If one uses synthetic polymer sealants like PUR types, the advice is to follow the recommendations from the manufacturer to obtain the best result as the author has seen many examples where other materials could do the job better.

The personnel interviewed in the two visited DIY centres had no suggestions for a non-chemical substitute for MDI-based foam sealants. Sealant bands were available in the store, but the function of these bands was to fill big gaps in the voids before using the sealant foam as a finishing, e.g. for insulation around window frames or sealing around tubes.

However, according to an expert interviewed, expanding sealant bands exist which can be used instead of sealants on MDI basis or other chemistry. This is confirmed in the DIY literature (Boile, 2007), which also present rules of thumb for the use of expanding sealant bands for DIYs regarding dimensions, cleaning of surfaces and handling in general. These bands are open cellular, which means that moisture can pass.

TABLE 1
SUGGESTIONS FOR NON-CHEMCIAL ALTERNATIVES

MDI-based product	Application	Non-chemical alternative identified	Pros	Cons
Coatings	Coating of concrete or wood surface such as floors or panels	For concrete: tiles instead of coating For wood: Pre-coated boards or panels	Reduce exposure for consumer Pre-treated boards and panels are easy to use.	Tiles and pre-treated woods can be expensive and not an option for all applications (particularly renovations). Tiles are also a time consuming option.
	Coating of plastics or metals	Laminated plastic and composite, prefabricated Pre-coated elements	Reduce exposure for consumer	Not possible for all applications. Not always applicable for renovations.
Adhesives	Mechanical joints between e.g. woods, concrete, plastic or metals	bolts, screws, nails etc.	Reduce exposure for consumer, easier to disconnect after installation if needed	Often considered more expensive and time consuming. Mechanical joints sometimes need to be combined with an adhesive to obtain required strength. Not always applicable for renovations.
	Joints between plastics, metals and glass	Heat welding, rivets, prefabricated rubber/plastic profiles	Reduce exposure for consumer	Not possible for all types of joints and materials and not for all applications. Welding at high temperature not considered relevant in a consumer scenario.
Sealants	Insulation and sealing foam e.g. between window frame and wall or for sealing around tubes.	- Expanding sealant bands. - Mineral wool and seal with lime mortar	Reduce exposure for consumer. Mineral wool/lime mortar is considered the best solution as sealants for windows.	Not as easy to use as available foaming products. Some bands need additional sealing. Not possible to paint over.

2.7 Results - Chemical alternatives

From visits to two DIY centres, it was found that the only MDI-based products for consumers found in both centres were MDI-based rigid PUR foams and there was no indication of the availability of coatings and adhesives based on MDI. Products available to the consumer through purchase in online web stores are plentiful and consumer exposure to MDI through this route is a possibility. As described earlier, a number of products (consumer targeted as well as other types) containing MDI, as well as isocyanate-free products through an internet search, have been identified.

For the purpose of this project, chemical alternatives have been categorised into six groups:

- Blocked or encapsulated MDI
- Aliphatic diisocyanates, free and blocked
- Prepolymer MDI
- Monomers for Non-isocyanate-based polyurethane (NIPU)
- Monomers for Hybrid non-isocyanate-based polyurethane (HNIPU)
- Monomers for other hybrid polymers based on silane chemistry

2.7.1 Input from stakeholders

The trade associations ISOPA[1], DFL[2], CEPE[3] and FEICA[4] were contacted with respect to their point of view on alternatives to MDI in products targeted coatings, adhesives and sealants intended for consumers.

ISOPA and DFL, who were also contacted in connection with the LOUS report, did not have any further details or other information relevant to a forwarded questionnaire on alternatives. Instead ISOPA referred to the downstream user organizations representing producers/formulators of the particular product types – CEPE and FEICA. DFL referred to the producers/formulators of these product types represented in Denmark. No response was received from CEPE or from FEICA within the time frame of the project.

11 companies either producing the chemical alternatives (two) or formulating/distributing sealants, coatings or adhesives for the consumer segment (nine) have been contacted to obtain detailed information. Four of the 11 companies were Danish formulators/distributors also contacted during the LOUS project, but not necessarily through the same contact person.

Three of the interviewed companies have phased out the use of MDI in consumer-targeted products today, but for the most part they could not give detailed information on the chemical composition of specific alternatives used to replace MDI-based systems. The reason was either that this is considered trade secrets or because of lack of precise information on the chemical composition of the raw materials used when formulating products.

One company is actively involved in development activities in the area of alternatives to MDI, but cannot share details due to confidentiality reasons.

Some companies pointed to the use of isocyanate products with reduced content of free MDI as a mean to reduce exposure for end users, e.g. using prepolymer MDI types. According to one source, this can also reduce the labelling requirements on the products. This confirms the findings in the LOUS report, which however also pointed to the fact the European isocyanate branch organisation (ISOPA) generally considers modified/prepolymeric MDIs as having the same hazards and labelling requirements as free MDI.

One formulator, which produce sealants (foams) and sell both MDI-based and STP-based products (silane terminated polyurethanes) to the professional segment, sees an increasing demand for alternatives to the MDI-based products in this marked and a slow but steady shift toward MDI free products. Today the marked share is estimated to approximately being evenly split between these two types. This might indicate an overall trend of a movement towards isocyanate free products, but no direct knowledge on the consumer segment was available from the formulator.

Manufacturers of chemical alternatives falling within the scope of alternatives in this project have shared information on specific alternatives, but do not hold detailed information on the exact end-uses and whether or not the products containing the alternatives are available to a consumer. The information shared will be incorporated in the description of each group of chemical alternatives where relevant.

[1] The European Diisocyanate and Polyol producers Association
[2] Danish Coatings and Adhesives Association (In Danish: Danmarks Farve- og Limindustri)
[3] European Council of the Paint, Printing Ink and Artists's Colourants
[4] Association of the European Adhesive & Sealant Industry

2.7.2 Blocked and encapsulated MDI

Blocked MDI
Chemistry behind
It is possible to modify the reactive group of MDI by blocking with other chemical agents that dissociate at higher temperatures and regenerate the isocyanate reactivity. Typically a weak reversible bond between the isocyanate and a hydrogen active group is formed.

Examples of blocking groups include: oximes, phenols, ε-caprolactam, malonester and triazoles (Oertel, 1983; Delebecq *et al.*, 2013). Such modifications will reduce the reactivity and toxicity of the isocyanates at temperatures below the regeneration temperature. The low reactivity of the blocked isocyanates also increases the pot life of the products. The pot life is the period of time a reacting composition remains suitable for its intended processing after mixing with reaction-initiating agents.

According to ISOPA, this blocking of the isocyanate group is only possible with isocyanates used for textiles, fibres and coatings (Christensen *et al.*, 2014).

According to Delebecq *et al.* (2013) high temperatures are usually needed for the de-blocking. The de-blocking temperatures are in the range 120-250°C or even higher. This is confirmed in technical datasheet from Bayer where a recommended reaction temperature for some (not waterborne) blocked isocyanates is in the range 175-180°C (Bayer MaterialScience, 2013b).

According to Delebecq *et al.* (2013), the most commonly used blocking agent for coating and painting is for example ε-caprolactam (CAS 105-60-2) which according to its harmonised classification causes skin irritation and serious eye irritation (ECHA, 2014).

Delebecq *et al.* (2013) describes the blocking mechanism for isocyanates in detail.

Assessment of availability for consumers
Suppliers of blocked MDI such as Bayer are present on the marked and supply a wide range of grades commercially (Bayer MaterialScience, 2013b). This is expected to reflect a commercial use, but no information on the wide-spread use in consumer products can be documented. Recommendations from the suppliers primarily include niche applications (e.g. activation at high temperature) and generally applications within the industry (Bayer MaterialScience, 2013b) most likely indicating a low consumer availability.

The conclusion on blocked diisocyanates is that due to the need for high temperature for the regeneration of the isocyanate reactivity, it is considered unrealistic that these can find use as alternatives to MDI in products meant for the consumer. This non-consumer use is also in line with available (although scarce) information regarding products on the marked.

It should be noted, that if one was to assess the health and environmental effects of blocked MDI in more detail, one should also consider the health effect of the blocking agent released when the temperature is increased.

Encapsulated MDI
Chemistry behind
Encapsulation, in which the reactive isocyanates are masked with a coat (a physical blocking), is another possibility to reduce exposure to the isocyanates and to increase the pot life of the product. This might find use in some adhesive and sealant applications (US Patent Application, 2006), but no further information on commercial products using encapsulated isocyanates has been identified during this survey.

Assessment of availability for consumers
No commercially available encapsulated MDI has been identified in this survey. Therefore no or low commercial use is expected.

2.7.3 Aliphatic diisocyanates

Other diisocyanates than the aromatic MDI and TDI are available commercially, mostly for special purpose urethane applications.

Free aliphatic diisocyanates
Chemistry behind
Hexamethylene diisocyanate (HDI) and 1-(isocyanatomethyl)-3,5,5-trimethyl-cyclohexan (IPDI) and bis(4-isocyanatocyclohexyl)methane (HDMI) are especially used for coatings and lacquer (Riddar J.B., 2013 and Delebecq *et al.*, 2013). These are aliphatic diisocyanates and according to literature their reactivity is most often inferior to the aromatic diisocyanates like MDI and for this reason cure time will be longer (Christensen *et al.*, 2014). The aliphatic diisocyanates show improved resistance to yellowing over time and as a consequence of environmental exposure (weathering) but aliphatic diisocyanates are also considered to be more expensive than aromatic diisocyanates (Christensen *et al.*, 2014; Xie *et al.*,2009; Madison Chemicals, not dated).

Conclusion on availability for consumers
The conclusion for aliphatic diisocyanates is that free types of aliphatic isocyanates have been identified on the market and are expected to find use mainly in industrial applications. Aliphatic isocyanates have some properties that make them preferable in some applications for coatings and lacquers such as reduced yellowing over time. They are however more expensive than MDI. Except in niche applications, free aliphatic diisocyanates are considered of very low use in consumer products.

Blocked aliphatic diisocyanates
Chemistry behind
Aliphatic diisocyanates can be blocked in the same manner as described for MDI (see Section 2.7.2). The most common blocking agent is caprolactam and the blocking reaction is in fact reversible. However a trick that can be used with respect to blocking of both aliphatic and aromatic isocyanates is to use ethyl acetoacetate as a blocking agent (forming an oxime derivative). This substance converts into a non-nucleophilic (unreactive) product 3-methylisoxazol-5-one after de-blocking making the reaction irreversible. The use of blocked aliphatic diisocyanates is expected to find use only in industrial applications and furthermore the reactivity of blocked MDI is found to be higher than blocked HDI (Delebecq *et al.*, 2013).

According to Delebecq *et al.* (2013) the aliphatic isocyanates are preferred in <u>*waterborne coatings*</u> due to this lower reactivity towards water as compared to MDI, and at the same time to prevent yellowing of the final coat. Ionizable groups (usually carboxyl introduced by the use of dimethylol propionic acid) can be used as blocking agents in an initial reaction with isocyanates. This blocking group will as a first step be incorporated into the polyurethane backbone and neutralized with carboxyl groups with a tertiary amine, before being dispersed in water thereby facilitating the formulation of a waterborne coating.

For such waterborne coatings, the PUR film is sometimes post cured with a polyisocyanate leading to isocyanate structures to obtain better mechanical properties. This is obtained by the use of a two-component system, which is not the preferred solution for a consumer because it is not as easy to use as a one-component system.

Some <u>*water-soluble systems*</u> are based on blocking with bisulphite adducts or sodium pyrosulfite. Bisulphite blocked isocyanates are mainly sensitive to pH variation rather than temperature increase. At high pH they hydrolyse and form symmetric ureas. Compared to de-blocking at very elevated temperatures, a de-blocking at high pH should be easier to handle for a consumer (at room temperature). However a high pH can also be undesirable for a consumer since exposure to a product with high pH can lead to skin irritation or corrosion. However, no such products have been identified in the course of this survey.

Conclusion on availability for consumers

From the information gathered in this survey, it seems that the free aliphatic diisocyanates are not as commonly used as the modified/blocked types (Uhlig, 1998). A range of blocked aliphatic diisocyanates are available commercially through Bayer. Again, this is expected to reflect a commercial use, but no information on the wide-spread use in consumer products can be documented. Recommendations from the suppliers primarily include applications within niche applications (e.g. reduced yellowing but higher price) and industrial applications (Bayer MaterialScience, 2013b) most likely indicating a low consumer availability. From the chemistry, it is concluded that aliphatic diisocyanates are primarily used for coatings and lacquers.

The conclusion for aliphatic diisocyanates is that blocked as well as free types of aliphatic isocyanates have been identified on the market and are expected to find use mainly in industrial applications. Aliphatic isocyanates have some properties that make them preferable in some applications for coatings and lacquers such as reduced yellowing over time and for blocked HDI a reduced reactivity compared to blocked MDI, which can be good for systems with a high content of water. They are however more expensive than MDI. Except in niche applications, blocked aliphatic diisocyanates are considered of low use in consumer products.

2.7.4 Prepolymer MDI

Chemistry behind

Prepolymeric MDI can be prepared from monomeric or polymeric MDIs via a catalysed partial reaction with themselves (creating an MDI homo-oligomer). ISOPA claims that prepolymeric MDI must be classified and labelled in line with the classification of monomeric MDI (Christensen *et al.*, 2014).

MDI-based prepolymers are prepared by reaction between MDI and hydroxyl-containing compounds such as polyols creating molecules still terminated with reactive aromatic isocyanate groups. The molecules contain a PUR backbone and at the same time contain free isocyanate groups for further polymerization and crosslinking. These MDI-based prepolymers are marketed by e.g. Bayer who writes in their marketing material that modified/prepolymer MDI with a low fraction of non-polymer bound components open up formulation options for the production of reactive polyurethane adhesives and sealants with reduced labelling requirements (Bayer MaterialScience, 2013b). As will be further elaborated in Chapter 3, this however does not seem to be the case for the most relevant prepolymer MDIs currently marketed.

Bayer's range of "polyisocyanates" comprises a broad range of products for 1 or 2 component polyurethane systems for a number of applications. The products are used by automotive original equipment manufacturers (OEM) for refinishing and coating of transportation vehicles, wood, industrial goods and plastics. They are also used in reactive adhesives, textile coatings and anti-corrosion coatings (Christensen *et al.*, 2014).

Conclusion on availability for consumers

MDI-based prepolymers are available commercially and are recommended for applications aimed at consumer use. Some indications are given via contact to manufacturers that these types of MDI-based prepolymers are used in products on the marked today in order to reduce the content of free MDI.

MDI-based prepolymeres are available e.g. from Bayer under the trade names 'Desmodur E' and 'Desmodur M'. Bayer recommends the prepolymeric MDI grades for a large range of applications within wood bonding, flexible packaging, binder for corrosion protection (Desmodur E), as well as sealants and elastic adhesives (Desmodur M). Bayer's range of prepolymers comprises a broad range of products for 1 or 2 component polyurethane systems for a number of applications. The products are used by OEM for refinishing and coating of transportation vehicles, wood, industrial goods and plastics as well as in reactive adhesives, textile coatings and anti-corrosion coatings.

2.7.5 Monomers for Non-Isocyanate-based Polyurethane (NIPU)

Chemistry behind

Polyurethane (PUR) can be produced without making use of aromatic diisocyanates resulting in Non-Isocyanate-based Polyurethane (NIPU). One alternative route is based on the reaction between cyclic carbonates and aliphatic and cycloaliphatic amines (such as 1,4-butane diamine (BDA), 1,6-hexamethylene diamine (HMDA), 1,12-dodecane diamine (DADO), and isophorone diamine (IPDA), diethylenetriamine (DETA)). This route to PUR has been known for the last 50 years, but this way of synthesizing non-isocyanate based PUR (NIPU) has not been practised industrially for different reasons such as low reactivity and decreased crosslinking density (Figovsky *et al.*, 2013).

Recent research has overcome the slow reaction e.g. by using multifunctional cyclocarbonates and aliphatic di- or tri-amines resulting in polyhydroxyurethanes (Figovsky *et al.*, 2012). According to Figovsky, a great problem of the NIPU technologies is the absence of commercially available multi-functional cyclic carbonates. However, some cyclic polycarbonates are offered commercially under the trade name Jeffsol by Huntsman (Huntsman, 2005) (see 2.7.6), who also own patents on the use of these substances in NIPU (US patent, 2013).

Another possible problem is that NIPU might have insufficient water resistance as the PUR formed is a polyhydroxyurethane polymer, however it is claimed that it is possible by proper formulation to make the NIPUs resistant to water (Figovsky *et al.*, 2012). The poor water resistance is due to the hydroxyl groups present in the polyhydroxyurethane polymer. The problem can be circumvented by copolymerization e.g. an acrylic epoxy oligomer and forming cyclocarbonate acrylic polymers with high water and weather resistance. A paint formulation with a curing temperature of 110°C and a curing time of 2-3 hours was obtained. Unfortunately the formulation requires the use of solvent (Figovsky *et al.*, 2012).

Javni (2008) has prepared a series of NIPUs by reacting vegetable oil based cyclic polycarbonates with some of the above mentioned aliphatic diamines and the effect of amine structure on mechanical and physical properties of the polyurethanes was studied.

The patent situation supports this judgement, as patents regarding NIPU have recently been applied for:

- Cyclic carbonate monomers and polymers prepared therefrom (US Patent Application, 2013)
- The synthesis of NIPU from renewable resources (US Patent Application, 2012).
- Method for preparing polyhydroxy-urethanes (US Patent, 2011)
- Non-isocyanate-based polyurethane and hybrid polyurethane-epoxy nanocomposite polymer compositions (US patent, 2013)

Exposure to isocyanates is eliminated by this route, as they are not used in the preparation of NIPUs. Delebecq *et al.* (2013) concludes that the best way to solve the toxicity problems associated with the diisocyanates is to substitute the diisocyanates with chemistry based on the cyclic polycarbonate-amine reaction to form the NIPU. However, it should be mentioned that the NIPUs are produced with rather reactive cyclic polycarbonates combined with amines and the toxicity, exposure and risks of all/both components have to be considered.

Information gathered during this mapping has made it possible to further asses the possibility to substitute MDI with cyclic carbonate based NIPU chemistry (Figovsky *et al.*, 2013; Delebecq *et al.*, 2013).

Figovsky *et al.* (2013) has made an overview of the recent publications in the recent advances in chemistry and technology of NIPU, including use of NIPU materials as coatings, adhesives and sealants. Primary attention is given to materials that contain epoxy and acrylic compounds. Hybrid organic-inorganic composites comprising of silanes are also considered (see Section 2.7.6).

The fundamentals for the practical applications of NIPU on the basis of five-membered cyclic carbonates (1,3-dioxolan-2-ones) in coatings, adhesives and sealants were largely developed by Figovsky *et al.* in the 1970 – 1980's. The NIPU networks forms a cross-linked polymer with β- hydroxyurethane groups - a polyhydroxyurethane polymer. Figovsky *et al.* claims that since NIPU is obtained without using isocyanate, the process of synthesis is relatively safe for both humans and the environment. Moreover this type of NIPU is not sensitive to moisture in the surrounding environment and the hydroxyl groups formed at the β-carbon atom of the urethane moiety also increase adhesion properties.

However, one problem which remains is that the inferior elasticity of NIPUs does not permit elastomeric applications (sealants and adhesives) and the mechanical properties and resistance to acids and bases are also not very good (Delebecq *et al.*, 2013).

Also NIPU use is restricted due to a low thermo stability of β-hydroxyurethanes. This low stability might be explained by the weakening of the bond between the carbonyl carbon and oxygen in the urethane group due to the influence of the OH-group (PCI, 2005).

Conclusion on availability for consumers
Monomers are available through e.g. Huntsman, but no information has been found on commercial products claiming use of NIPU technology. Some draw backs are expected to limit the possible applications, so low/no consumer use is expected.

The conclusion about alternatives within NIPUs is that some monomers are available commercially and that the NIPUs can be used for some applications. The applicability of NIPUs as an alternative to MDI-based products has its limitations due to lower thermal stability, lower elasticity and lower water resistance and no consumer use is expected.

2.7.6 Monomers for Hybrid Non-Isocyanate-based Polyurethane (HNIPU)

Chemistry behind
Hybrid Non-Isocyanate based Polyurethanes (HNIPU) are composites comprising urethane units as well as e.g. functional silanes, polysiloxanes, epoxy resins and amine hardeners (Figovsky *et al.*, 2013). To belong to the HNIPU category urethane units must be present in the polymer.

The problem with low thermo stability and lack of elasticity of β-hydroxyurethanes (NIPU) can be solved by using aminosilanes and cyclocarbonates whereby thermo stable compounds (HNIPU) are achieved.

According to Delebecq *et al.* (2013), another way to circumvent this drawback (low thermo stability) is to make use of HNIPU based on the epoxy-amine-cyclocarbonate oligomers to build at network structure.

Polymate Ltd. has developed a HNIPU based on hydroxyl-amine adducts on the base of aliphatic mono-and polycyclic carbonates as hardeners (Figovsky *et al.*, 2013). Figovsky *et al.* also mentions silane-containing and nano-structured hydroxyurethane compounds. This includes hybrid organic-inorganic compositions of epoxy resins, amine hardeners, functional silanes, and/or polysiloxanes and they cure in the presence of water in an amount sufficient to bring about substantial hydrolytic polycondensation of the silane (Figovsky *et al.*, 2013). Some of the more complicated formulations for HNIPU make use of silane chemistry. Such nanostructured hybrid polymer compositions was synthesized on the basis of epoxy-multifunctional compositions, cyclic carbonate components, amine-functional components and acrylate (methacrylate) functional component, where at least one of the components contains alkoxysilane units. The cure rate is fast at 10-30°C under the formation of nanostructure based on a hydrolytic polycondensation of the alkoxysilanes by means of atmospheric moisture creating an organic-inorganic nanostructure. The cured composition has excellent strength-stress properties, adhesion to a variety of substrates, an improved appearance, and resistance to weathering, abrasion, and solvents (Figovsky *et al.*, 2013).

A patent (US patent, 2007) describes NIPU and HNIPU foams and coatings based on epoxies, acrylic epoxies, acrylic cyclocarbonates, acrylic hydroxyurethane oligomers, and bifunctional amines. However, all these compositions are used “in-place” (*in situ*) and are unsuitable for spray applications due to longer durations of gelation and solidification, which can lead to flow on vertical surfaces and collapse of the foam before setting. No commercial application has been identified in this survey.

The German company EFM Gmbh have produced novel non-isocyanate nanostructured polyurethane binders for monolithic flooring and industrial paint. It is claimed that the two component binders combine the best mechanical properties of polyurethane with the chemical resistance of epoxy (PCI, 2005).

Nanotech Industries claims that their product Green Polyurethane™ is the first-ever modified hybrid polyurethane, currently used in coatings and paint, manufactured without the use of toxic isocyanates throughout the entire production process (NTI, 2014). Polyoxypropylene triols and epoxydized vegetable oils are used as raw materials for the preparation of Green Polyurethane™. They claim that it can substitute conventional polyurethane and epoxies and is much less toxic, have superior properties and provides 30 – 60% in application costs.

Green Polyurethanes has been developed into commercially available coatings, which are currently being sold world-wide and pilot samples of Green Polyurethane foam, adhesives and sealants are at present being tested for commercialization. The focus of the development is not consumer products but it is mentioned that the product can be used for private and public garages in coating application and can be cured without heating.

Figovsky *et al.* points to a number of other developments needed to increase the applicability and use of NIPU/HNIPU: the development of waterborne HNIPU formulations, NIPU formulations for sealants and adhesives, development of production of amines modified with hydroxyurethane groups and elaboration of non-amine room temperature curing agents for oligomeric compositions among others proposals.

Bayer produces silane terminated polyurethanes in a range of shore hardness (Bayer MaterialScience, 2013a), which can be used to produce HNIPU. The silane terminated polyurethanes of this type of HNIPU have a polyurethane backbone based on isocyanate chemistry and therefore do not have the drawbacks of the hydroxypolyurethane backbone.

Conclusion on availability for consumers
Bayer offer Silane terminated polyurethanes in a range of shore hardness according to application for sealing or as adhesive (Bayer MaterialScience, 2013a), but no information on use in consumer products have been documented.

The conclusion about alternatives within HNIPU is that some raw materials are available commercially and are recommended for consumer relevant applications such as sealants and adhesives. The applicability of HNIPUs as an alternative to MDI-based products is expected to be higher than for NIPU alternatives.

2.7.7 Monomers for other hybrid polymers based on silane chemistry

Chemistry behind

Silane terminated polymers (such as MS-polymers – silyl modified polyether) and organofunctional silanes are commercially available from e.g. Wacker Silicones (Wacker Silicones, 2005) and SiSiB Silanes (SiSiB Silicones, not dated).These can be similar to HNIPU polymers, but do not contain polyurethane units in the backbone and therefore do not fall under the HNIPU categories.

Wacker (not dated) claims to exploit the benefits of α-silanes in the development of innovative general-purpose adhesives and sealants to replace numerous polyurethane counterparts in the construction industry. The company has a long list of different α-silanes with different reactive functional groups attached. New products based on α-silanes are claimed to offer the same or even better properties and to have no known harmful effects (Wacker Silicones, 2005).

For sealants, it might for instance be possible to replace polyurethane with a silylmodified polyether (an MS polymer) based on α-silane chemistry (silane terminated polyether), which has very good flexible and weathering properties (Petrie, 2010).

Standard γ-silane terminated polymers have a relatively slow crosslinking rate due to the molecular structure of the terminal silyl group compared to the newest developed commercial α-alkoxy silane terminated polymers (α-silanes). In the α-silanes, the electron donor is attached to the silicon atom via a short hydrocarbon chain - a methylene group. With this configuration, the alkoxy groups are activated, so that the crosslinking reaction is accelerated considerably. This enhanced reactivity is the decisive difference between the α- and γ–silanes. The spacer in the γ–silanes is a longer hydrocarbon chain e.g. a linear propylene group which means that the electron donor is further away from the silicon atom and the effect on the speed of crosslinking in the presence of moisture is lower than for the α-silanes (Wacker Silicones, 2005)

The basic chemistry for hybrid polymers containing silanes is based on highly reactive α-alkoxysilanes, which can have different functional groups depending on the function of the silanes and cure upon contact with humidity. During the reaction with water vapour (humidity) the alkoxygroups split of methanol. The high reactivity is retained even if the α-silane group is attached to organic polymers.

Difunctional alkoxysilanes (used for MS-polymers) have the advantage that they release less methanol during crosslinking than the trialkoxysilanes. On the other hand, a lower cross-linking density is obtained with the dialkoxisilanes, thus favouring the formation of a more elastic product (Bayer MaterialScience, 2013c).

Alpha-silanes can be used in sealant and adhesive formulations not only as cross-linkers, but also as valuable compounding additives. Formulations based on silane terminated polymers are typically protected against pre-curing by the addition of vinyltrimethoxy-silane or other reactive silanes. The function is as water scavenger to avoid gelling upon storage.

The α-silanes are as mentioned highly reactive and the curing speed can be adjusted by the choice of catalyst system, and even tin-free catalyst systems are possible (e.g. amines). An advantage of the silanes is their low viscosity, which makes it possible to fine tune the curing kinetics. By using α-silanes, it is possible to close the gap between silicone sealants and polyurethane systems in terms of their mechanical properties.

The synthetic routes to silane terminated polymers are either the aminosilane route or the isocyanate route. The aminosilane route gives higher viscosity and higher modulus (hydrogen bridges) and the isocyanate route gives lower viscosity and lower modulus.

Bayer has made the following comparison between HNIPU based on their silane terminated polyurethanes (as mentioned in Section 2.7.6) and MS-polymers included in the category of other hybrid polymers (Bayer MaterialScience, 2013c):

- HNIPU have better mechanical properties (higher elastic recovery/better creep resistance)
- HNIPU have faster cure due to the use of trifunctional silanes making it possible to use amine instead of tin catalyst
- HNIPU have a PUR backbone and silicone endcapping which gives improved adhesion
- HNIPU give a big variety of building blocks and synthetic routes making it possible to make tailored solutions.

However, for some applications, the MS polymers seem to be the preferred choice as they are easily available for the consumers.

Conclusion on availability for consumers
Products based on hybrid polymers containing silane chemistry, but not PUR units in the backbone, such as MS-polymers are commercially available through internet shops as well as DIY centres under different brand names within sealant (elastic and rigid foams) and adhesives applications. Some products claim content of the MS-polymer, while others use different terminology for similar chemistry such as hybrid polymer, SMX, STP or SiMP, since MS-polymer is a registered trademark.

The conclusion on hybrid polymers containing silane chemistry is that there seems to be a lot of activity in the area and that some chemical alternatives (monomers) for this type of chemistry are commercially available today. It looks like the area is growing and there are a lot of products on the marked with this type of chemistry within consumer applications (adhesives and sealants).

2.8 Summary of findings

2.8.1 Identified non-chemical alternatives

Overall, non-chemical alternatives are scarce. The possibility for non-chemical solutions will depend on which type of material or combination of material is used in the application and whether the product is to be used for renovation or new installations. Table 1 shows suggested non-chemical alternatives for some applications. Expanding sealant bands is judged to be a possible replacement for sealant foams in some instances, but it is expected that the consumer in most cases will use expanding foam due to the ease of use. Other non-chemical routes are to use factory made products coated or glued before distribution to consumers. Mechanical joints such as nails, spikes, screws, tongue/groove and rivets are possible for a number of applications, but are often combined with the use of adhesives to strengthen the bonds between materials. Most of the identified non-chemical alternatives are more applicable in relation to new installations than for repair/renovation.

2.8.2 Identified chemical alternatives

Only MDI sealant foams were recognized at the shelves in two DIY centres, however a range of consumer and professional products for coatings, adhesives and sealants containing MDI or MDI alternatives were identified through an internet based search.

The survey has identified a broad range of chemical alternatives to MDI (monomers, prepolymers etc.) intended for use in coatings, adhesives and sealants (elastic and rigid foams), which to some extent are or could be available to consumers. The identified alternative substances have been arranged into six categories of alternatives. An overview of the identified categories is given in Table

2. A list of specific chemical products identified is shown in Table 3. For some alternatives, the CAS number is not available (e.g. for some of Bayer's products).

The most promising substitution seems to be for rigid foam sealants, where commercial alternatives exist.

2.8.3 Prioritisation and choice of alternatives for health and environmental assessment

In Table 3, a suggested prioritisation for monomers selected for health assessments in this project is given (last column of the table). A rating from 1 – very low priority to 4 –very high priority is given. The priority is set based on which MDI-containing consumer products have been identified on the marked today, as well as the expected commercial availability of the alternatives based on the information gathered in this survey. Highest priority is given if the alternative chemistry is considered easily available to the consumer and has been identified in consumer products on the marked or is recommended by a supplier for consumer relevant applications. Lowest priority is given if the alternative chemistry is considered an emerging technology and no specific link to use of the chemistry in products on the marked has been identified. In agreement with the Danish EPA, substances with high priority (priority 4) have been chosen for the further work in this project.

Blocked diisocyanates are not included in the next phase of the project (priority 1), since these do not seem easily applicable for consumer use due to high temperatures (as well as special equipment needed for de-blocking). Further, it should be noted that blocking agent are released upon deblocking (leading to exposure).

Aliphatic diisocyanates are not included in the next phase of the project, since these are only recommended for industrial or niche applications not intended for consumers (priority 1).

Prepolymer MDIs are available and are recommended by suppliers for consumer relevant applications, so these are included in the next phase of the project (priority 4).

Selected NIPU monomers are interesting, since these are commercially available and based on an expert opinion possibly find use in some consumer applications in spite of no clear marketing of the use of NIPU technology for consumer products as such. NIPUs based on the identified monomers are only considered an emerging technology (although some find use as precursors for HNIPU) and are therefore not included in the next phase of the project.

For the siliane terminated polymers, both polyether (other hybrid polymers based on silane chemistry) and polyurethane (HNIPU) based backbone grades are chosen for further study, since this is a technology already on the marked and is present in the following types of consumer products: adhesives, elastic sealants and sealant foams. Both types are frequently mentioned in the literature and in connection with products identified through an internet search.

A number of these are recommended by Wacker for use in consumer relevant products (these are given priority 4), but no information regarding the grades SiSiB PC 1210, 2300, 2310 and 3500 in Table 3 has been available and these are therefore given a low priority (priority 2).

TABLE 2
OVERVIEW OF ALTERNATIVE CHEMISTRIES IDENTIFIED IN THE SURVEY

Chemical alternative	Description of chemistry	Typical composition or choice of monomer	Pros and cons	Expected consumer availability
Blocked and encapsulated MDI	MDI or other isocyanate is blocked through bond to blocking agent which prevents access to the reactive group of the isocyanate	Isocyanate blocked with groups such as oximes, phenols, ε-caprolactam, malonester and triazoles.	Pro: Reduce exposure to free isocyanate at room temperature. Long pot life. Reactivity restored under controlled conditions (temperature or pH) Cons: Reactivity is restored upon de-blocking. Blocking agent as well as isocyanate is released on de-blocking and consumer exposed to both.	A
Aliphatic diisocyanates	Aliphatic diisocyanates	Aliphatic diisocyanates, primarily used as blocked, prepolymerised or blended.	Pro: Less yellowing, low reactivity preferred in some applications. Lower toxicity expected. Cons: Price – they are more expensive. Reactivity lower – can't be used in all applications.	B
Prepolymer MDIs	Reaction products of diisocyanates with less free (reactive) isocyanate groups	Higher molecular weight than free isocyanates, but otherwise the same basic chemistry	Pro: Prepolymerization reduces the number of free isocyanate groups and a reduction in toxicity might therefore be expected. Cons: There is no consensus regarding toxicity, since ISOPA says it should be considered as toxic as free isocyanates, whereas some suppliers claim reduced need for labelling.	B/C
Non-isocyanate-based polyurethane (NIPU)	Mostly the polyhydroxy-urethanes are studied.	Mostly the combination of cyclocarbonates with amines have been studied	Pros: Can be used for some applications and monomers seem to be commercially available. Cons: Has its limitations due to lower thermal stability, lower elasticity and lower water resistance.	A
Hybrid non-isocyanate-based polyurethane (HNIPU)	Composites comprising urethane units as well as other functional groups.	Several composites possible comprising e.g. functional silanes, polysiloxanes, epoxy resins and amine hardeners.	Pros: High activity in the area and many monomers for this type of chemistry are commercially available today. They solve some of the problems with the NIPU materials because of higher elasticity. Cons: Price in higher than the MDI based products (price index 1.5-3)[1].	B/C
Other hybrid polymers based on silane chemistry	MS-polymer (silyl modified polyether)		Pros: Commercially available today. Can replace MDI based sealants (elastic and rigid foams) and adhesives. Cons: Price is higher than the MDI based products.	C/D

Letters in the last column designate:
A: commercial available, not applicable in consumer products
B: commercial available, may potentially be used in consumer products
C: some commercial available consumer products identified
D: consumer products with the alternative is common in the market
[1] Personal communication, Wacker Silicones.

TABLE 3
IDENTIFIED ALTERNATIVES TO MDI IN COATINGS, ADHESIVES AND SEALANTS

Trade name	Supplier	Product chemistry	Application(s)	CAS no	Comments	Priority (low 1- 4 high)
Blocked MDI						
Desmodur ® BL 3175 SN	Bayer	Blocked HDI polyisocyanate	Coatings (auto, industrial, coil, can and glass)	85940-94-9	Aliphatic, light stable and weather resistant. Standard product but not consumer relevant application. Bayer brochure. Also contains: CAS 64742-95-6 (25%)	1
Desmodur ® BL 4265 SN	Bayer	Blocked IPDI polyisocyanate	Coatings (auto, industrial, coil, can and glass)	Not available	Aliphatic, light stable and weather resistant. Standard product but not consumer relevant application. Bayer brochure. Also contains: CAS 64742-95-6 (35%). Precautionary mention on SDS: 2-butanone oxime < 0,1w% CAS 96-29-7. No consumer relevant application.	1
Desmodur ® BL 5375	Bayer	Blocked HMDI polyisocyanate	Coatings (industrial, coil, can)	Not available	Aliphatic, light stable and weather resistant. High flexibility. Contain: Solvent naphtha ca. 12,5% CAS: 64742-95-6 and 2-methoxy-1-methylethyl acetate ca. 12,5% CAS: 108-65-6 and 2-butanone oxime < 1% CAS: 96-29-7. No consumer relevant application.	1
Desmodur ® BL 3475 BA/SN	Bayer	Diethyl malonate blocked HDI/IPDI polyisocyanate	Coatings (industrial, coil, can)	Not available	Aliphatic, light stable and weather resistant. High reactivity. Also contain: n-Butyl acetate ca. 12,5% CAS: 123-86-4 and solvent naphtha ca. 12,5% CAS 64742-95-6. No consumer relevant application.	1
Crelan ® NI-2	Bayer	Cycloaliphatic diisocyanate adduct masked with caprolactam (blocked branched IPDI polyisocyanate)	Coatings (powder coatings)	Not available	Economical standard powder coatings. Also contains: caprolactam < 5% CAS: 105-60-2. Precautionary mentioned on SDS: Isophorone Diisocyanate < 0,1% CAS: 4098-71-9 No consumer relevant application.	1
Aliphatic diisocyanates						
Hexamethylene diisocyanate (HDI)	e.g. Bayers Desmodur	Free HDI	Coating and sealants	822-06-0	Aliphatic isocyanates. Reduced yellowing over time compared to MDI. Identified as a common aliphatic isocyanate (US EPA, 2011). No consumer relevant application.	1
Isophorene diisocyanate (IPDI)	e.g. Bayers Desmodur	Free IPDI	Coating and sealants	4098-71-9	Aliphatic isocyanates. Reduced yellowing over time compared to MDI. Identified as a common aliphatic isocyanate (US EPA, 2011). No consumer relevant application.	1
bis(4-		Free Methylene-bis(4-		5124-30-1	No consumer relevant application.	1

Trade name	Supplier	Product chemistry	Application(s)	CAS no	Comments	Priority (low 1- 4 high)
isocyanatocyclohex-yl)methane (HDMI)		cyclohexylisocyanate)				
Desmodur® N100		Biuret HDI	Weather stable and non-yellowing coat-ing	Not availa-ble	No consumer relevant application.	2
Desmodur® N75 MPA/X		Biuret HDI	Wood, furniture, industrial and plastic coatings.	Not availa-ble	Anti-yellowing, anti-corrosion and chemical resistant coatings. No consumer relevant application.	2
MDI-based prepolymers						
Desmodur® E 23	Bayer	Aromatic polyisocyanate prepolymer based on MDI (mixture)	Adhesive (wood bonding, binder for corrosion protection), flexible packaging, metal coating	Mixture of: 60%: CAS-no 99784-49-3 20%: CAS-no 5873-54-1 20%: CAS-no 101-68-8	Consumer relevant application.	4
Desmoseal® M 280	Bayer	Aromatic prepolymer based on MDI (mixture)	Sealants, elastic adhesives	Mixture of: 80% CAS-no: 59675-67-1 <5%: CAS-no 101-68-8 Ca. 0.5%: CAS-no: 4083-64-1	Consumer relevant application.	4
Monomers for non-isocyanate-based polyurethane (NIPU) (a)						
Jeffsol ® EC	Huntsman	ethylene carbonate	Primarily coatings	96-49-1	Reacts with amines to produce β-hydroxyalkyl ure-thanes, EC/PC mix also available. Available commer-cially and might find use in consumer products.	3
Jeffsol ® PC	Huntsman	propylene carbonate	Primarily coatings	108-32-7	Reacts with amines to produce β-hydroxyalkyl ure-thanes, EC/PC mix also available. Available commer-cially and might find use in consumer products.	3
Jeffsol ® BC	Huntsman	butylene carbonate	Primarily coatings	4437-85-8	Reacts with amines to produce β-hydroxyalkyl ure-thanes. Available commercially and might find use in	3

Trade name	Supplier	Product chemistry	Application(s)	CAS no	Comments	Priority (low 1- 4 high)
					consumer products.	
Jeffsol ® GC	Huntsman	Glycerine carbonate	Primarily coatings	NA?	Reacts with amines to produce β-hydroxyalkyl urethanes. Available commercially and might find use in consumer products.	3
Carbalink ® HPC	Huntsman	Hydroxy propyl carbamate	Primarily coatings	69493-47-6	Reacts with amines to produce β-hydroxyalkyl urethanes. Can give dihydroxy functionality on reaction to amines (increase cross-linking). Also contain CAS no. 57-55-6 propylene glycol and CAS no. 108-32-7 propylene carbonate. Available commercially and might find use in consumer products.	3
BDA		1,4-butane diamine (BDA)	Primarily coatings	110-60-1	Reacts with cyclic carbonates to produce β-hydroxyalkyl urethanes. Available commercially and might find use in consumer products.	3
HMDA		1,6-hexamethylene diamine (HMDA)	Primarily coatings	124-09-4	Reacts with cyclic carbonates to produce β-hydroxyalkyl urethanes. Available commercially and might find use in consumer products.	3
DADO		1,12-dodecane diamine (DADO)	Primarily coatings	2783-17-7	Reacts with cyclic carbonates to produce β-hydroxyalkyl urethanes. Available commercially and might find use in consumer products.	3
IPDA		isophorone diamine (IPDA)	Primarily coatings	2855-13-2	Reacts with cyclic carbonates to produce β-hydroxyalkyl urethanes. Available commercially and might find use in consumer products.	3
DETA		diethylenetriamine (DETA)	Primarily coatings	111-40-0	Reacts with cyclic carbonates to produce β-hydroxyalkyl urethanes. Available commercially and might find use in consumer products.	3
Monomers for hybrid non-isocyanate-based polyurethane (HNIPU)						
Desmoseal ® S XP 2636	Bayer	Silane terminated prepolymers (STP) - Hybrid systems of PUR with reactive silane end groups	Adhesives, sealants (low modulus with high elongation)	Not available (mixture)	Available and STP based consumer products identified.	4
Desmoseal ® S XP 2458	Bayer	Silane terminated prepolymers (STP) - Hybrid systems of PUR with reactive silane end groups	Adhesives (high modulus, medium elongation)	Not available (mixture)	Available and STP based consumer products identified.	4
Desmoseal ® S XP 2749	Bayer	Silane terminated prepolymers (STP) - Hybrid systems of PUR with reactive silane end groups	Adhesives (plasticizer free with high hardness)	Not available (mixture)	Available and STP based consumer products identified.	4

Trade name	Supplier	Product chemistry	Application(s)	CAS no	Comments	Priority (low 1- 4 high)
Monomers for other hybrid polymers based on silane chemistry						
SiSiB® PC1100	Nanjing SiSiB Silicones Co. (China)	3-Aminopropyltriethoxysilane (aminosilan)	Adhesives, sealants and coatings	919-30-2	Recommended for thermosets for PU. According to SiSiB silicones this is comparable to Geniosil GF93 from Wacker. Recommended for consumer relevant application.	4
SiSiB® PC1200	Nanjing SiSiB Silicones Co. (China)	N-(2-Aminoethyl)-3-Aminopropyltrimethoxysilane (amino silane)	Adhesives, sealants and coatings	1760-24-3	Recommended for thermosets for PU. According to SiSiB silicones this is comparable to Geniosil GF9 / 91 from Wacker. Recommended for consumer relevant application.	4
SiSiB® PC1210	Nanjing SiSiB Silicones Co. (China)	N-(2-Aminoethyl)-3-Aminopropyltriethoxysilane (amino silane)	Adhesives and sealants	5089-72-5	Recommended for thermosets for PU. According to SiSiB silicones this is comparable to Geniosil GF94 from Wacker. No further knowledge on consumer applications.	2
SiSiB® PC2300	Nanjing SiSiB Silicones Co. (China)	3-Mercaptopropyltrimethoxysilane (mercapto silanes)	Adhesives and sealants	4420-74-0	Recommended for thermosets for PU. According to SiSiB silicones this is comparable to Geniosil GF 70 from Wacker. No further knowledge on consumer applications.	2
SiSiB® PC2310	Nanjing SiSiB Silicones Co. (China)	3-Mercaptopropyltriethoxysilane (mercapto silanes)	Adhesives and sealants	14814-09-6	Recommended for thermosets for PU. No further knowledge on consumer applications.	2
SiSiB® PC3500	Nanjing SiSiB Silicones Co. (China)	2-(3,4-Epoxycyclohexyl)-ethyltrimethoxysilane (epoxy silanes)	Adhesives and sealants	3388-04-3	Recommended for thermosets for PU. No further knowledge on consumer applications.	2
Geniosil® STP-E10	Wacker	Dimethmethoxy(methyl)silylmethylcarbamate-terminated polyether (alpha-silane)	Adhesives, sealants (and coatings)	611222-18-5	Higher methoxygroup content than E30. Available and recommended for consumer relevant application by Wacker.	4
Geniosil® STP-E30	Wacker	Dimethmethoxy(methyl)silylmethylcarbamate-terminated polyether (alpha-silane)	Construction adhesives, construction sealants, flooring adhesives, industrial adhesives (and coatings)	611222-18-5	Available and recommended for consumer relevant application by Wacker.	4
Geniosil® STP-E35	Wacker	Trimethoxysilylpropylcarbamate-terminated polyether	Adhesives, sealants and coatings	216597-12-5	Available and recommended for consumer relevant application by Wacker.	4

Trade name	Supplier	Product chemistry	Application(s)	CAS no	Comments	Priority (low 1- 4 high)
Geniosil® STP-E15	Wacker	Trimethoxysilylpropyl-carbamate-terminated polyether	Adhesives, sealants and coatings	216597-12-5	Higher methoxygroup content than E35. Available and recommended for consumer relevant application by Wacker.	4
Geniosil® XB502	Wacker	silane-terminated binder based on alpha-silane technology (alpha-silane)	Adhesives, sealants and coatings	Not available	Available and recommended for consumer relevant application by Wacker.	4
Geniosil® GF 9 (a)	Wacker	N-(2-Aminoethyl)-3-aminopropyltrimethoxysilane (Amino functionalised silane)	Adhesives, sealants and coatings	1760-24-3	DIY consumer application mentioned on Wackers homepage. Mentioned combination with STP-E's and XB 502 in technical datasheet. Work as adhesion promoter.	4
Geniosil® GF 93 (a)	Wacker	3-Aminopropyltriethoxysilane (Amino functionalised silane)	Adhesives, sealants and coatings	919-30-2	DIY consumer application mentioned on Wackers homepage. Work as adhesion promoter.	4
Geniosil® GF 95 (a)	Wacker	N-(2-Aminoethyl)-3-aminopropylmethyl-dimethoxysilane (Amino functionalised silane)	Adhesives, sealants and coatings	3069-29-2	DIY consumer application mentioned on Wackers homepage. Work as adhesion promoter.	4
Geniosil® GF 96 (a)	Wacker	3-Aminopropyltri-methoxysilane (Amino functionalised silane)	Adhesives, sealants and coatings	13822-56-5	DIY consumer application mentioned on Wackers homepage. Work as adhesion promoter.	4
Geniosil® GF 98 (a)	Wacker	3-Ureidopropyltri-methoxysilane (Amino functionalised silane)	Adhesives, sealants and coatings	23843-64-3	DIY consumer application mentioned on Wackers homepage. Work as adhesion promoter.	4
Geniosil® GF 80 (a)	Wacker	3-Glycidoxypropyltri-methoxysilane (Epoxy functionalised silane)	Adhesives, sealants and coatings	2530-83-8	DIY consumer application mentioned on Wackers homepage. Work as adhesion promoter.	4
Geniosil ® XL 10 (a)	Wacker	Vinyltrimethoxysilane	Adhesives, sealants and coatings	2768-02-7	Used in small amounts together with GF 9 and STPs as a water scavenger (reduce pre-curing, increase pot life)	4
(a) Monomers also find use in HNIPU						

In agreement with the Danish EPA, priority 4 substances have been chosen for the health and environmental assessment. The chosen substances are listed in Table 4 below. In the table, it is also indicated whether a substance is considered a "main monomer", an "adhesion promoter" or a "water scavenger". One substance can be either water scavenger or adhesion promoters depending on the product composition and application.

TABLE 4
SUMMARY OF PRIORITY 4 SUBSTANCES (MONOMERS) AS ALTERNATIVES FOR MDI IN COATINGS, ADHESIVES AND SEALANTS TARGETED CONSUMERS

Trade name	Product chemistry	Application(s)	CAS no	Comments
MDI-based prepolymers				
Desmodur® E 23	Polyisocyanate prepolymer based on MDI	Adhesive (wood bonding, binder for corrosion protection), flexible packaging, metal coating	Mixture of 99784-49-3, 5873-54-1, 101-68-8	Consumer relevant application. MAIN MONOMER
Desmoseal® M 280	Aromatic prepolymer based on MDI	Sealants, elastic adhesives	Mixture of 59675-67-1, 4083-64-1, 101-68-8	Consumer relevant application. MAIN MONOMER
Monomers for hybrid non-isocyanate-based polyurethane (HNIPU)				
Desmoseal ® S XP 2636	Silane terminated prepolymers (STP) - Hybrid systems of PUR with reactive silane end groups	Adhesives, sealants (low modulus with high elongation)	Mixture, not available	Available and STP based consumer products identified. MAIN MONOMER
Desmoseal ® S XP 2458	Silane terminated prepolymers (STP) - Hybrid systems of PUR with reactive silane end groups	Adhesives (high modulus, medium elongation)	Mixture, not available	Available and STP based consumer products identified. MAIN MONOMER
Desmoseal ® S XP 2749	Silane terminated prepolymers (STP) - Hybrid systems of PUR with reactive silane end groups	Adhesives (plasticizer free with high hardness)	Mixture, not available	Available and STP based consumer products identified. MAIN MONOMER
Monomers for other hybrid polymers based on silane chemistry				
Geniosil® STP-E10 /30	Dimethmethoxy(methyl)silylmethylcarbamate-terminated polyether (alpha-silane)	Adhesives, sealants (and coatings)	611222-18-5	Higher methoxygroup content than E30. Available and recommended for consumer relevant application by Wacker. MAIN MONOMER
Geniosil® STP-E15/35	Trimethoxysilylpropylcarbamate-terminated polyether	Adhesives, sealants and coatings	216597-12-5	Available and recommended for consumer relevant application by Wacker. MAIN MONOMER
Geniosil® XB502	silane-terminated binder based on alpha-silane technology (alpha-silane)	Adhesives, sealants and coatings	Not available	Available and recommended for consumer relevant application by Wacker. MAIN MONOMER

Geniosil® GF 9 / SiSiB® PC1200	N-(2-Aminoethyl)-3-aminopropyltri-methoxysilane (Amino functional-ised silane)	Adhesives, sealants and coatings	1760-24-3	DIY consumer application mentioned on Wackers homepage. Mentioned combination with STP-E's and XB 502 in technical datasheet. Work as AD-HESION PROMOTOR.
Geniosil® GF 93 / SiSiB® PC1100	3-Aminopropyl-triethoxysilane (Amino functional-ised silane)	Adhesives, sealants and coatings	919-30-2	DIY consumer application mentioned on Wackers homepage. Work as AD-HESION PROMOTOR.
Geniosil® GF 95	N-(2-Aminoethyl)-3-aminopropylmethyl-dimethoxysilane (Amino functional-ised silane)	Adhesives, sealants and coatings	3069-29-2	DIY consumer application mentioned on Wackers homepage. Work as AD-HESION PROMOTOR.
Geniosil® GF 96	3-Aminopropyl-trimethoxysilane (Amino functional-ised silane)	Adhesives, sealants and coatings	13822-56-5	DIY consumer application mentioned on Wackers homepage. Work as AD-HESION PROMOTOR.
Geniosil® GF 98	3-Ureidopropyl-trimethoxysilane (Amino functional-ised silane)	Adhesives, sealants and coatings	23843-64-3	DIY consumer application mentioned on Wackers homepage. Work as AD-HESION PROMOTOR.
Geniosil® GF 80	3-Glycidoxypropyl-trimethoxysilane (Epoxy functional-ised silane)	Adhesives, sealants and coatings	2530-83-8	DIY consumer application mentioned on Wackers homepage. Work as AD-HESION PROMOTOR.
Geniosil ® XL 10	Vinyltrimethox-ysilane	Adhesives, sealants and coatings	07-02-2768	Used in small amounts together with GF 9 and STPs as a WATER SCAV-ENGER (reduce pre-curing, increase pot life) as well as ADHESION PROMOTOR

3. Health and environmental assessment of chemical alternatives

3.1 Scope and approach

3.1.1 Overview of alternatives assessed

This Chapter addresses the "priority 4" chemical alternatives identified in Chapter 2, see Table 3 and Table 4. These include two prepolymer MDI alternatives, three HNIPU monomer alternatives and 10 alternatives belonging to the group 'other hybrid polymers based on silane chemistry' (will be abbreviated 'other hybrid silane' in this chapter). An overview of alternatives is provided in Table 5.

TABLE 5
OVERVIEW OF CHEMICAL ALTERNATIVES ADDRESSED (PRIORITY 4 FROM CHAPTER 2)

Alternative type	Identification	Chemical Name (Trade name example(s))
MDI-based pre-polymer	Mixture Components: 60%: CAS-no 99784-49-3 20%: CAS-no 5873-54-1 20%: CAS-no 101-68-8	Polymeric diphenylmethane diisocyanate (Desmodur® E 23) Aromatic polyisocyanate prepolymer = o-(p-isocyanatobenzyl)phenyl isocyanate MDI
MDI-based pre-polymer	Mixture Components: 80% CAS-no: 59675-67-1 <5%: CAS-no 101-68-8 Ca. 0.5%: CAS-no: 4083-64-1	Polymeric diphenylmethane diisocyanate (Desmoseal® M 280) Diphenylmethanediisocyanate-prepolymer MDI p-Toluenesulfonyl isocyanate
HNIPU monomer	Mixture Component IDs not available, but according to SDS no dangerous ingredient are contained.	"prepolymer with silane end groups" or "solvent-free silane-terminated polyurethane prepolymer" (Desmoseal ® S XP 2636)
HNIPU monomer	Mixture Component IDs not available, but according to SDS no dangerous ingredient are contained.	"prepolymer with silane end groups. ca. 90 % in Alkyl Sulfonic acid Phenolate" or "solvent-free silane-terminated polyurethane prepolymer" (Desmoseal ® S XP 2458)

Alternative type	Identification	Chemical Name (Trade name example(s))
HNIPU monomer	Mixture Component IDs not available, but according to SDS no dangerous ingredient are contained.	"prepolymer with silane end groups" or "solvent-free silane-terminated polyurethane prepolymer" (Desmoseal ® S XP 2749)
Other hybrid silane, main monomer	CAS-no: 611222-18-5	Dimethoxy(methyl)silylmethylcarbamate-terminated polyether (alpha-silane) (Geniosil® STP-E10) (Geniosil® STP-E30)
Other hybrid silane, main monomer	CAS-no: 216597-12-5	Trimethoxysilylpropylcarbamate-terminated polyether (Geniosil® STP-E35) (Geniosil® STP-E15)
Other hybrid silane, main monomer	Not available	(Geniosil® XB502)
Other hybrid silane, adhesion promoter	CAS-no: 919-30-2	3-aminopropyltriethoxysilane (SiSiB® PC1100) (Geniosil® GF 93)
Other hybrid silane, adhesion promoter	CAS-no: 1760-24-3	N-(2-Aminoethyl)-3-Aminopropyltrimethoxysilane (amino silane) (SiSiB® PC1200) (Geniosil® GF 9)
Other hybrid silane, adhesion promoter	CAS-no: 3069-29-2	N-(2-Aminoethyl)-3-aminopropylmethyldimethoxysilane (Amino functionalised silane) (Geniosil® GF 95)
Other hybrid silane, adhesion promoter	CAS-no: 13822-56-5	3-Aminopropyltrimethoxysilane (Amino functionalised silane) (Geniosil® GF 96)
Other hybrid silane, adhesion promoter	CAS-no: 23843-64-3	3-Ureidopropyltrimethoxysilane (Amino functionalised silane) (Geniosil® GF 98)

Alternative type	Identification	Chemical Name (Trade name example(s))
Other hybrid silane, adhesion promoter	CAS-no: 2530-83-8	3-Glycidoxypropyltrimethoxysilane (Epoxy functionalised silane) (Geniosil® GF 80)
Other hybrid silane, water scavenger as well as adhesion promoter	CAS-no: 2768-02-7	Vinyltrimethoxysilane (Geniosil ® XL 10)

3.1.2 Approach

This chapter will address the identified alternatives in four groups:

- Prepolymer MDIs
- Monomers for HNIPU
- Monomers for other hybrid polymers based on silane chemistry (main monomers)
- Monomers for other hybrid polymers based on silane chemistry (adhesion promoters)

The two latter are used together and the comparative assessment with MDI-based products thus takes main monomer as well as adhesion promoters into account.

Thus, this chapter will address these groups in three sections, the latter with sub-sections for 'other hybrid silane' main monomers and promoters, respectively. An overall conclusion will be presented in Chapter 4.

For each group, the inherent properties of identified alternatives will be compared with MDI-based on their classification and physico-chemical properties, and where needed further hazard data (toxicity, environmental fate and ecotoxicity) will be collected.

Actual risks of the alternatives (as compared to MDI) not only depend on the inherent properties of alternatives and MDI, but also on exposure, including how the alternative is applied and in which amounts. Further, the other components of an adhesive, coating or sealant product are crucial for the overall hazard and risk, see also Section 3.1.3 below. It has been outside the scope of the current study to assess risks in detail, but some considerations based on the available information will be provided.

The identified prepolymer MDIs and HNIPU monomer alternatives are mixtures and in particular for the latter, little information regarding composition is available. Consequently, the Safety Data Sheets has been the main information source for these mixtures.

For the remaining alternatives, i.e. the 10 alternatives based on 'other hybrid silane' chemistry, information has been searched in the following sources:

- ECHA[5] dissemination site summarising inherent property information form REACH registration dossiers (http://echa.europa.eu/information-on-chemicals/registered-substances)
- ECHA classification and labelling inventory (http://echa.europa.eu/uk/information-on-chemicals/cl-inventory)

[5] European Chemical Agency

- ESIS[6] (http://esis.jrc.ec.europa.eu/)
- IPCS[7], WHO[8], IARC[9] via INCHEM (http://www.inchem.org/)
- OECD via Echem portal (http://www.echemportal.org/echemportal/index?pageID=0&request_locale=en)
- ATSDR[10] (www.atsdr.cdc.gov)
- Safety Data Sheets from suppliers

3.1.3 Consumer exposure scenarios

The current project investigates possible differences between applying MDI and alternative monomer chemistry, respectively, in coatings, adhesives and sealants, which could be used by consumers.

It is not expected that consumers will apply MDI-based products (or alternatives) in actual spraying applications. Thus in general, the most relevant exposure routes are expected to be dermal (possibly eye) exposure to the product ingredients and inhalation exposure to volatile ingredients. To this end, it should be noted that MDI (as opposed to e.g. TDI) has a very low vapour pressure and will not evaporate under normal conditions.

However, sealants can for some purposes (sealant foams) be provided in pressurized cans with various solvents as propellant gases. This could lead to inhalation of not only contained solvents and propellants gases, but also to aerosolised ingredients which would normally not evaporate.

A 10 year old study looked into the chemistry and provided some exposure observations for a range of sealants (Nilsson *et al.*, 2004). An exposure experiment was carried out with an MDI containing PU foam sealant. The foam was applied to glass plates for a period of 10 minutes. The person applying the foam was equipped with MDI-filters in the breathing zone. The MDI content was subsequently quantified using HPLC[11]. No MDI was detected and given the detection limit, it was concluded that average air concentration in the breathing zone was below 1 µg/m^3 during the application period. These data indicate that MDI inhalation exposure resulting from applying MDI foam sealants could be very low or non-existent.

Thus, inhalation exposure seems to be associated with volatile ingredients in the products. In relation to foam sealants, the report finds that MDI-based foam sealants typically contain 'light hydrocarbons' and dimethyl ether, whereas methanol and small amounts of acetone, hexane and other C6-hydrocarbons was found in the sealants based on 'other hybrid silane' chemistry (Nilsson *et al.*, 2014). The 'other hybrid silane' foam sealant formulations were generally labelled to contain <0.2% (w/w) methanol, whereas analytical quantification in one product showed about 3.6% (w/w) methanol. This makes sense as these products are known to split off methanol (hydrolysis) during use.

No methanol exposure measurements were conducted in the study, but measurements were made on silicone sealants known to split off butanone-2-oxim during use. Various sampling methods were used to quantify the butanone-2-oxim formed during use/application. Inhalation exposures ranging from below 0.5 mg/m^3 (no solvent found above detection limit on charcoal sampling tube) and 4.4 mg/m^3 (on DNPH[12] sampling tube) were estimated.

If these values are roughly taken as an indication of the possible methanol split off from foam sealants based on 'other hybrid chemistry', there could be a significant methanol exposure during application. It should however be stressed that the rate of solvent split off from sealants depends on

[6] European chemical Substances Information System
[7] International Programme on Chemical Safety
[8] World Health Organization
[9] International Agency for Research on Cancer
[10] Agency for Toxic Substances and Disease Registry
[11] HPLC: High-performance liquid chromatography
[12] DNPH: Dinitrophenylhydrazine

temperature, humidity, amount applied etc. and that one of the sampling methods in the Nilsson *et al.* (2004) report did not find detectable solvent amounts in inhalation samples.

In relation to other co-formulants, it can be noted that MDI-based sealants were found to contain 5-10% chlorinated paraffin's, whereas some of the sealants based on 'other hybrid chemistry' were found to contain phthalates (4.2% DEHP[13] in one type and 32% diisodecylphthalate in another type). 0.5% dibutyltin was found as preservative in one sealant for marine purposes.

It should be stressed that the report referred is 10 years old and that only a limited number of products where examined analytically for content and exposure potential.

Thus an updated survey and wider analytically experiments would be needed to draw more firm conclusions in relation to the current situation.

Nevertheless, the following considerations/indications can be extracted:

- It does not seem that MDI is released to the breathing zone when using MDI-based sealant foams
- There could be a relatively high methanol inhalation exposure when using 'other hybrid silane' chemistry sealants (methanol split off during use)
- Exposure to organic solvents can occur during use of foam sealants based on MDI as well as those based on 'other hybrid chemistry'. Nature and amount of organic solvent should be considered on a case-by-case basis when comparing two products
- A 10 year old report indicated that chlorinated paraffin's (MDI-based sealants) and phthalates ('other hybrid silane' chemistry sealant) were, among others, used as co-formulants. Again, the complete list of sealant co-formulants would have to be considered when comparing two products

3.1.4 MDI

As a baseline, information regarding physico-chemical properties and classification of MDI has been extracted from the LOUS report, see Table 6 and Table 7.

TABLE 6
PHYSICOCHEMICAL DATA FOR MDI (AS TAKEN FROM CHRISTENSEN ET AL., 2014)

Property	MDI
Molecular weight	250.3 g/mol
Physical state	Ranging from dark amber viscous liquid to white waxy solid
Melting point	2,4'-MDI: 34-38°C 4,4'-MDI: 39-43°C Polymeric MDI: 5°C
Boiling point	> 300 °C
Relative density	4,4'-MDI: 1.325 Polymeric MDI: 1.2381
Vapour pressure (20°C)	2,4'-MDI: 0.0014 Pa 4,4'-MDI: 0.002 Pa Polymeric MDI: 0.005 Pa ------ "MDI": 0.0004 Pa

[13] DEHP: Di(2-ethylhexyl) phthalate

Property	MDI
Vapour pressure (40°C) **Vapour pressure (80°C)**	"MDI": 0.006 Pa "MDI": 2 Pa
Surface tension	NA, since substance will react with water
Water solubility (mg/l)	Due to the high reactivity of the NCO group with water, current EC standard methods cannot be used. Based on calculations, a worst case value of 0.02 mg/l was used for the EU risk assessment.
Log P (octanol/water)	Measured to 4.5, but considered irrelevant due to the transient existence of MDI in water

TABLE 7
HARMONISED CLASSIFICATION OF MDI ISOMERS ACCORDING TO ANNEX VI OF REGULATION (EC) NO 1272/2008 (CLP REGULATION) (AS TAKEN FROM CHRISTENSEN ET AL., 2014)

Index No	International Chemical Identification	CAS No	Classification	
			Hazard Class and Category Code(s)	Hazard statement Code(s)
615-005-00-9	2,2'-methylenediphenyl diisocyanate (2,2'-MDI)	2536-05-2	Carc. 2 Acute Tox. 4 * STOT RE 2 * Eye Irrit. 2 STOT SE 3 Skin Irrit. 2 Resp. Sens. 1 Skin Sens. 1	H351 H332 H373** H319 H335 H315 H334 H317
615-005-00-9	o-(p-isocyanatobenzyl)phenyl isocyanate (2,4'-MDI)	5873-54-1	Carc. 2 Acute Tox. 4 * STOT RE 2 * Eye Irrit. 2 STOT SE 3 Skin Irrit. 2 Resp. Sens. 1 Skin Sens. 1	H351 H332 H373** H319 H335 H315 H334 H317
615-005-00-9	4,4'-methylenediphenyl diisocyanate (4,4'-MDI)	101-68-8	Carc. 2 Acute Tox. 4 * STOT RE 2 * Eye Irrit. 2 STOT SE 3 Skin Irrit. 2 Resp. Sens. 1 Skin Sens. 1	H351 H332 H373** H319 H335 H315 H334 H317
615-005-00-9	Methylenediphenyl diisocyanate (mix of MDI isomers)	26447-40-5	Carc. 2 Acute Tox. 4 * STOT RE 2 * Eye Irrit. 2 STOT SE 3 Skin Irrit. 2 Resp. Sens. 1 Skin Sens. 1	H351 H332 H373** H319 H335 H315 H334 H317

* Use of "*" in connection with a hazard category (e.g. Acute Tox. 4 *) implies that the category stated shall be considered as a minimum classification.

** Use of "**" in connection with a hazard statement code (e.g. H373**) implies that the route of exposure is not specified.

Further, in relation to environmental fate, it was found that when released to water, MDI (and TDI) will readily immobilise.

3.2 Prepolymer MDI alternatives

3.2.1 Inherent properties

The two prepolymer MDI alternatives identified are supplied by Bayer. According to the Safety Data Sheets, these products are considered mixtures, see also Table 5. Hazard classification and information on physico-chemical properties and environmental fate parameters for these two mixtures as taken from the Safety Data Sheets is summarised in Table 8 and Table 9, respectively.

TABLE 8
CLASSIFICATION ACCORDING TO CLP AS TAKEN FROM SAFETY DATA SHEETS FOR THE TRADE NAMES INDICATED

Alternative type	Identification/name (Trade name)	Hazard Class and Category Code(s)	Hazard statement Code(s)
MDI-based prepolymer	Mixture / Polymeric diphenylmethane diisocyanate (Desmodur® E 23)	Skin Irrit. 2 Skin Sens. 1 Eye Irrit. 2 Acute Tox 4 Resp. Sens. 1 STOT SE 3 Carc. 2 STOT RE 2 Aquatic Chronic 2	H315 H317 H319 H332 H334 H335 H351 H373 H411
MDI-based prepolymer	Mixture / Polymeric diphenylmethane diisocyanate (Desmoseal® M 280)	Skin Irrit. 2 Skin Sens. 1 Eye Irrit. 2 Acute Tox 4 Resp. Sens. 1 STOT SE 3 Carc. 2 STOT RE 2	H315 H317 H319 H332 H334 H335 H351 H373

TABLE 9
PHYSICOCHEMICAL AND ENVIRONMENTAL FATE PROPERTIES FOR PREPOLYMER MDI ALTERNATIVES AS TAKEN FROM SAFETY DATA SHEETS FOR THE TRADE NAMES INDICATED

Physicochemical properties	Desmodur E 23	Desmodur M 280
Physical state	Liquid	Liquid
Melting point	No information provided in SDS	No information provided in SDS
Boiling point (°C)	Not applicable, degrades	> 200
Relative density (g/cm³)	1.13	1.07

Physicochemical properties	Desmodur E 23	Desmodur M 280
Vapour pressure (Pa)	4100 at 50°C	9000 at 50°C
Surface tension	No information provided in SDS	No information provided in SDS
Water solubility (mg/L)	Not water soluble	Not water soluble
Log P (octanol/water)	Not established	Not established
Environmental fate properties		
Hydrolysis/reaction with water	DT_{50}: 20 h at 25°C (read-across from comparable product)	DT_{50}: 20 h at 25°C (read-across from comparable product)
Photodegradation	DT_{50} (air): 0.92 d (read-across from comparable product)	DT_{50} (air): 0.92 d (read-across from comparable product)
Biodegradation	0% in 28d, i.e. not biodegradable	0% in 28d, i.e. not biodegradable (read-across from comparable product)
Bioaccumulation	BCF = 200 (read-across from comparable product)	BCF = 200 (read-across from comparable product)

3.2.2 Assessment of inherent properties

As can be seen from Table 7 and Table 8, the two MDI prepolymers are classified for the same properties as MDI. This is in line with information from the isocyanate branch organisation (ISOPA[14]) given to the LOUS project indicating that classification and hazards for prepolymers should be the same as that of "pure" MDI.

3.2.3 Exposure and risk considerations

The classification of prepolymer MDIs might have been driven by the content of free MDI (and other isocyanates) in the mixtures, indicated to be 40% (20+20) for Desmodur E23 and about 5% for Desmoseal M 280. Thus, one could consider that exposure to free MDI monomers would be less in these prepolymers. However, when examining the Safety Data Sheets, it appears that the prepolymer content in these mixtures (60 and 80%, respectively) are also classified for these properties. Thus, it appears that inherent properties for "pure" MDI and prepolymer MDIs are rather similar.

Exposure could differ due to differences in vapour pressure. According to the data indicated in the Safety Data Sheets, the vapour pressure of the prepolymer MDI mixtures (4100 to 9000 Pa at 50°C) are considerably higher than the for MDI (0.006 Pa at 40 °C and 2 Pa at 80 °C). There may be a typo as it is indicated in the Safety Data Sheets for the prepolymer MDIs that the vapour pressure for the MDI monomers is very low. In any case, the vapour pressure for MDI even at 80 °C is very

[14] The European Diisocyanate and Polyol producers Association

low and it must be assumed that MDI will practically not evaporate. Thus for consumer uses (expected to take place at reasonable temperatures, see also discussion in Chapter 2), there is no indication that MDI will lead to higher exposures than prepolymer MDIs; possibly the opposite is the case given the vapour pressures indicated for the prepolymer MDIs.

No information has been identified regarding different amounts of materials needed in the formulations when applying MDI and prepolymer MDIs, respectively. However, it may be assumed that amounts are comparable.

Similarly, one might expect that product formulations (adhesives, coatings, sealants) applying MDI and prepolymer MDIs are rather similar with regards to these substances.

Overall, one could argue that the partly polymerisation in prepolymer MDIs would give less exposure to free MDI monomers, but based on the available information, this does not seem to lead to any significant difference in hazards and exposure and thereby risks. Thus, all in all, it does not appear that consumer products applying prepolymer MDIs would constitute any significant difference in hazards, exposures and thereby risks as compared with products based on pure MDI monomers.

3.3 Monomers for Hybrid Non-Isocyanate Polyurethane (HNIPU)

The three HNIPU monomer alternatives identified are all mixtures supplied by Bayer. The three products are described as "prepolymer with silane end groups" or "solvent-free silane-terminated polyurethane prepolymer".

3.3.1 Inherent properties

For all three alternatives, the Safety Data Sheets indicate that no classification is needed – in line with the statement that no dangerous substances are contained.

The physico-chemical, environmental fate, toxicity and ecotoxicity properties as available from the Safety Data Sheets are summarised in Table 10.

TABLE 10
PHYSICOCHEMICAL, ENVIRONMENTAL FATE, TOXICITY AND ECOTOXICITY PROPERTIES FOR HNIPU ALTERNATIVES AS TAKEN FROM SAFETY DATA SHEETS FOR THE TRADE NAMES INDICATED

Trade name	Desmoseal SXP 2636	Desmoseal SXP 2458	Desmoseal SXP 2749
Physicochemical properties			
Physical state	Liquid	Liquid	Liquid
Melting point (°C)	No information provided in SDS	No information provided in SDS	No information provided in SDS
Boiling point (°C)	300	No information provided in SDS	>300
Relative density (g/cm³)	1.01	1.02	1.01
Vapour pressure (Pa)	700 at 20°C 1300 at 50°C 1500 at 55°C	1500 at 20°C 3000 at 50°C 3400 at 55°C	700 at 20°C 2300 at 50°C 2600 at 55°C

Trade name	Desmoseal SXP 2636	Desmoseal SXP 2458	Desmoseal SXP 2749
Surface tension	No information provided in SDS	No information provided in SDS	No information provided in SDS
Water solubility (mg/L)	Not water soluble (at 15°C)	Not water soluble (at 15°C)	Not water soluble (at 15°C)
Log P (octanol/water)	Not established	Not established	Not established
Environmental fate properties			
Hydrolysis/reaction with water	No information provided in SDS	No information provided in SDS	No information provided in SDS
Photodegradation	No information provided in SDS	No information provided in SDS	No information provided in SDS
Biodegradation	"No data available"	Not readily biodegradable (Read-across from comparable product)	No information provided in SDS
Bioaccumulation	No information provided in SDS	No information provided in SDS	No information provided in SDS
Ecotoxicological information			
Acute Fish toxicity, 96h ***Brachydanio rerio/Danio rerio* (Zebra barbell)** **(OECD TG 203)**	LC50 > 100 mg/l (Read-across from comparable product)	LC50 > 100 mg/l (Read-across from comparable product)	LC50 > 100 mg/l (Read-across from comparable product)
Acute toxicity for daphnia, 48h ***Daphnia magna* (Water flea)** **(OECD TG 202)**	No toxic effect with saturated solution (Read-across from comparable product)	No toxic effect with saturated solution (Read-across from comparable product)	No toxic effect with saturated solution (Read-across from comparable product)
Acute toxicity for algae, 72h ***Scenedesmus subspicatus/ Desmodesmus subspicatus*** **(OECD TG 201)**	ErC50 > 100 mg/l (Read-across from comparable product)	ErC50 > 100 mg/l (Read-across from comparable product)	ErC50 > 100 mg/l (Read-across from comparable product)

Trade name	Desmoseal SXP 2636	Desmoseal SXP 2458	Desmoseal SXP 2749
Acute bacterial toxicity **Activated sludge** **(OECD TG 209)**	No information provided in SDS	EC50 > 10,000 mg/l (Read-across from comparable product)	EC50 > 10,000 mg/l (Read-across from comparable product)
Toxicological information			
Acute toxicity, oral rat (OECD TG 423)	LD50 > 2500 mg/kg (Read-across from comparable product)	LD50 > 2500 mg/kg (Read-across from comparable product)	LD50> 2500 mg/kg (Read-across from comparable product)
Skin irritation, rabbit (OECD TG 404)	Non-irritant (Read-across from comparable product)	Non-irritant (Read-across from comparable product)	Non-irritant (Read-across from comparable product)
Mucosae irritation, rabbit (OECD TG 405)	No eye irritation (Read-across from comparable product)	No eye irritation (Read-across from comparable product)	No eye irritation (Read-across from comparable product)
Skin sensitization (local lymph node assay (LLNA)), mouse (OECD TG 406)	Negative (Read-across from comparable product)	Negative (Read-across from comparable product)	Negative (Read-across from comparable product)
Genotoxicity in vitro, salmonella/microsome with and without metabolic activation (OECD EG 471)	Negative (Read-across from comparable product)	Negative (Read-across from comparable product)	Negative (Read-across from comparable product)

3.3.2 Assessment of inherent properties

It should be noted that the following assessment is based purely on information in the reviewed Safety Data Sheets for the three Desmoseal HNIPU alternatives investigated.

According to the Safety Data Sheets for the three alternatives, they do not contain any dangerous components according to the classification criteria and the mixtures are consequently not classified as dangerous. For all three products, toxicological and ecotoxicological test data are provided based on read-across from a "comparable product". These data indicate low toxicity and ecotoxicity.

Data on environmental fate are not provided for two of the products, whereas it is indicated that Desmoseal SXP 2458 is "Not readily biodegradable". This seems logic and is probably the case for all/most components of polymers. The lack of data might be due to immobilisation just as for MDI.

All in all, based on information provided in the Safety Data Sheets, it is concluded that HNIPU alternatives are considerably less inherently toxic as compared to MDI.

3.3.3 Exposure and risk considerations

The vapour pressures indicated for the investigated HNIPU alternatives (1000-3000 Pa between 20 and 55 °C) are much higher than for MDI (0.006 Pa at 40 °C and 2 Pa at 80 °C). However, this vapour pressure is still rather low (about the same as for water) and it is noted that the HNIPU alternatives are solvent free and do not contain any dangerous substances. Thus application of the HNIPU monomer in itself does not seem to lead to any significant inhalation exposure.

As concluded in Section 2.7.6, it might be that HNIPU could be used in sealant and adhesive consumer products. No information on differences in amounts of HNIPU and MDI, respectively needed for such applications have been identified. Further, no information on which co-formulants would be needed for producing adhesives, coating and sealants have been identified.

Overall, it is assessed that consumer risks could be reduced significantly if the assessed HNIPU alternatives substitute MDI in products used by consumers.

It should however be stressed that this assessment is based on:

- Limited knowledge about the composition of the HNIPU monomers (claimed to contain "no dangerous substances" in the supplier Safety Data Sheets) and consequently, the assessment is based solely on information in the supplier Safety Data Sheets
- Limited knowledge about which co-formulants, including possible organic solvents, would be needed in addition to the HNIPU monomers for formulating adhesives, coatings and sealants.

3.4 Monomers for other hybrid polymers based on silane chemistry

This section will first address main monomers including a comparison with MDI, then adhesion promoters including a comparison with MDI and finally products based on 'other hybrid silane' (containing main monomers, promoters and other co-formulants) will be addressed in comparison with MDI-based products.

3.4.1 Monomers for other hybrid polymers based on silane chemistry ("main monomers")

Three "main monomers" belonging to this group have been identified and prioritised in this survey (see Chapter 2). Chemical identification of one of these main monomers has not been available for this project, whereas the other two are identified in terms of CAS-numbers. These CAS numbers are however not registered under REACH. The reason for this has not been possible to clarify within the scope of this project, but could be: i) lack of marketing in Europe, ii) registration with another CAS number or as a UVCB[15] substance, or iii) considered outside the scope of REACH if fulfilling the polymer definition. Consequently, in this project, their properties will be described based on information in the Technical and Safety Data Sheets.

Inherent properties

Hazard classification for the three 'main monomers' based on 'other hybrid silane' chemistry is presented in Table 11 based on information in Safety Data Sheets.

Similarly, information on inherent properties as taken from the Safety Data Sheets is given in Table 12.

15 UVCB: Substances of Unknown or Variable composition, Complex reaction products or Biological materials

TABLE 11
CLASSIFCAITON FOR "OTHER HYBRID SILANES, MAIN MONOMERS" AS TAKEN FROM SAFETY DATA SHEETS FOR THE TRADE NAMES INDICATED

CAS No.	International chemical identification (Trade name example(s))	Hazard Class and Category Code(s)	Hazard statement Code(s)
611222-18-5	Dimethoxy(methyl)silyl-methylcarbamate-terminated polyether (alpha-silane) (Geniosil® STP-E10) (Geniosil® STP-E30)	No substances to be classified according to supplier, but hydrolyses under formation of methanol (CAS no. 67-56-1). Methanol has following hazard classes and codes: Flam Liq. 2 Acute Tox. 3 Acute Tox. 3 Acute Tox. 3 STOT SE 1	Methanol has following hazard statement codes: H225 H301 H311 H331 H370
216597-12-5	Trimethoxysilylpropyl-carbamate-terminated polyether (Geniosil® STP-E35) (Geniosil® STP-E15)	No substances to be classified according to supplier. Other hazards: Product hydrolyses under formation of methanol (CAS no. 67-56-1). Methanol has following hazard classes and codes: Flam Liq. 2 Acute Tox. 3 Acute Tox. 3 Acute Tox. 3 STOT SE 1	Methanol has following hazard statement codes: H225 H301 H311 H331 H370

CAS No.	International chemical identification (Trade name example(s))	Hazard Class and Category Code(s)	Hazard statement Code(s)
Not available	(Geniosil® XB502)	No substances to be classified according to supplier. Other hazards: Product hydrolyses under formation of methanol (CAS no. 67-56-1). Methanol has following hazard classes and codes: Flam Liq. 2 Acute Tox. 3 Acute Tox. 3 Acute Tox. 3 STOT SE 1	Methanol has following hazard statement codes: H225 H301 H311 H331 H370

TABLE 12
PHYSICOCHEMICAL, ENVIRONMENTAL FATE, TOXICITY AND ECOTOXICITY PROPERTIES FOR HNIPU ALTERNATIVES AS TAKEN FROM SAFETY DATA SHEETS FOR THE TRADE NAMES INDICATED

Substance	Dimethoxy (methyl)silylmethylcarbamate-terminated polyether (alpha-silane)	Trimethoxysilylpropylcarbamate-terminated polyether	Not available
Trade name example	Geniosil STP-E10, Geniosil STP-E30	Geniosil STP-E35, Geniosil STP-E15	Genisiol XB 502
Cas no.	611222-18-5	216597-12-5	Not available
Physicochemical properties			
Physical state	Liquid	Liquid	Liquid
Melting point (°C)	< -100 (STP-E10) Not applicable (STP-E30)	Not applicable	Not applicable
Boiling point (°C)	346 (STP-E10) Not applicable (STP-E30)	Not applicable	Not applicable
Relative density (g/cm³)	1.0069 (STP-E10) 1.002 (STP-E30)	1.0064 (STP-E15) 1.005 (STP-E35)	1.13

Substance	Dimethoxy (methyl)silylmethylcarbamate-terminated polyether (alpha-silane)	Trimethoxysilylpropylcarbamate-terminated polyether	Not available
Vapour pressure (Pa)	Not applicable	Not applicable	Not applicable
Surface tension	No information provided in SDS	No information provided in SDS	No information provided in SDS
Water solubility (mg/L)	STP-E10: < 10 STP-E30: Not applicable	STP-E35: Virtually insoluble STP-E15: Not applicable	Insoluble at 25°C
Log P (octanol/water)	STP-10: No information provided in SDS, but the following organic solvent solubility provided: > 500 g/l (23°C, in cyclohexane). STP-E30: No information provided in SDS	No information provided in SDS	No information provided in SDS
Environmental fate properties			
Hydrolysis /reaction with water	Contact with water liberates methanol and silanol- and/or siloxanol-compounds	Contact with water liberates methanol and silanol- and/or siloxanol-compounds	Contact with water liberates methanol and silanol- and/or siloxanol-compounds
Photo-degradation	No information provided in SDS	No information provided in SDS	No data known
Biodegradation (OECD 301F)	Water: 12% in 28 d, i.e. not readily biodegradable (Read-across from comparable product) Methanol formed by hydrolysis is readily degradable Silicone content eliminated by absorption to activated sludge.	Water: 12% in 28 d, i.e. not readily biodegradable (Read-across from comparable product) Methanol formed by hydrolysis is readily degradable Silicone content eliminated by absorption to activated sludge.	No data known Methanol formed by hydrolysis is readily degradable Silicone content eliminated by absorption to activated sludge.
Bioaccumulation	No data known	No data known	No data known

Substance	Dimethoxy (methyl)silylmethylcarbamate-terminated polyether (alpha-silane)	Trimethoxysilylpropylcarbamate-terminated polyether	Not available
Ecotoxicological information			
Acute Fish toxicity, 96h ***Oncorhynchus mykiss* (rainbow trout)**	LC50 > 100 mg/l (Read-across from comparable product)	LC50 > 100 mg/l (Read-across from comparable product)	No test data available
Acute toxicity for daphnia, 48h ***Daphnia magna* (Water flea)**	EC50 > 100 mg/l (Read-across from comparable product)	EC50 > 100 mg/l (Read-across from comparable product)	No test data available
Acute toxicity for algae, 72h ***Desmodesmus subspicatus***	IC50 > 100 mg/l (Read-across from comparable product)	IC50 > 100 mg/l (Read-across from comparable product)	No test data available
Acute bacterial toxicity **Activated sludge**	EC20 > 1000 mg/l (Read-across from comparable product)	EC20 > 1000 mg/l (Read-across from comparable product)	No test data available
Toxicological information			
Acute toxicity, oral	LD50 > 2000 mg/kg (Read-across from comparable product)	LD50> 2000 mg/kg (Read-across from comparable product)	Acute toxicity estimate (ATE) > 2000 mg/kg (Read-across from comparable product)
Acute toxicity, dermal	LD50 > 2000 mg/kg (Read-across from comparable product)	> 2500 mg/kg (Read-across from comparable product)	No test data available
Repeated toxicity, rat, oral (gavage) 28d, 7days/week (OECD 407)	NOAEL ≥ 500 mg/kg (Read-across from comparable product)	NOAEL: 500 mg/kg (Read-across from comparable product)	No test data available
Skin corrosion/irritation	No data known	Mildly irritating (due to adhesive properties)	No test data available
Eye damage/irritation	No data known	Study not technical feasible/not irritating	No test data available

Substance	Dimethoxy (methyl)silylmethylcarbamate-terminated polyether (alpha-silane)	Trimethoxysilylpropylcarbamate-terminated polyether	Not available
		(Read-across from comparable product)	
Skin sensitization (Magnusson-Kligman), guinea pig (OECD TG 406)	Negative (Read-across from comparable product)	Negative (Read-across from comparable product)	No test data available
Germ cell mutagenicity (bacterial mutation assays in vitro (OECD EG 471)	Negative (Read-across from comparable product)	Negative (Read-across from comparable product)	No test data available

Assessment of inherent properties
It should be noted that the following assessment is based purely on information in the reviewed Safety Data Sheets for the Geniosil alternatives investigated.

According to the Safety Data Sheets, these main monomers do not contain any dangerous components according to the classification criteria and the mixtures are consequently not classified as dangerous.

For all three products, toxicological and ecotoxicological test data are provided based on read-across from a "comparable product". These data indicate low toxicity and ecotoxicity of the monomers as such.

However, methanol might be released when in contact with water, e.g. if used in moisture/dampness conditions and/or in the gastro-intestinal tract if swallowed. Methanol is classified as toxic via all exposure routes (inhalation, oral and dermal) and has a severe classification for organ toxicity (STOT SE 1, H370: Causes damage to organs) due to its inherent properties of generating visual disorders including possible blindness. Please also refer to Section 3.1.3 regarding methanol split off when using 'other hybrid silane' chemistry as reactive monomer.

Hydrolysis of the monomers is of course also relevant in relation to environmental fate. However, the methanol amounts possibly released to the environment are assumed to be relatively minor and methanol is easily biodegradable (methanol is not classified for environmental hazards).

The STP-E polymers (and possibly also XB 502) as such are indicated to be "Not readily biodegradable". This seems logic and is probably the case for all/most components of polymers. The lack of data might be due to immobilisation just as for MDI.

No other data on environmental fate are identified.

All in all, based on information provided in the Safety Data Sheets, it is concluded that the "main monomers" of 'other hybrid silane' chemistry appear in themselves as having considerably less inherent toxicity as compared to MDI. However, methanol might be split off during use, which might be an issue for consumers, but is not expected to cause any significant problems for the environment.

3.4.2 Monomers for other hybrid polymers based on silane chemistry ("adhesion promoters")

Seven adhesion promoters based on "other hybrid silane" chemistry have been identified, see Table 5. Six of these have been registered under REACH.

Inherent properties

The classification for the seven adhesion promoters is provided in Table 13. One of the substances is subject to harmonised EU classification, whereas classification for the remaining six substances is taken from the classification and labelling inventory on the ECHAs web-site. These are self-classifications provided by any manufacturer/importer of the substance on its own or as part of a mixture. As the lead registrant is expected to possess most information about a give substance, the lead registrant's self-classification is highlighted in bold. Further, the number of notifiers supporting a given classification is also indicated, as well as the total number of notifiers.

The inherent properties of the seven alternatives are provided in Table 14. Sources of information are indicated in the table; for the six registered substances the main information source has been the ECHA dissemination site, whereas the Safety Data Sheet has been the main source for the not (yet) registered 3-Ureidopropyltrimethoxysilane.

Assessment of inherent properties

For only one of the substances (the water scavenger and adhesion promoter vinyltrimethoxysilane), a classification for possible carcinogenicity is suggested, but only by 32 out of 865 notifiers. Thus in general, these alternatives are not classified for (possible) carcinogenicity as is MDI.

Two of these adhesion promoters are suggested to be classified for skin sensitization (just like MDI). For one substance (N-(2-Aminoethyl)-3-Aminopropyltrimethoxysilane), the classification is supported by the lead registrant, whereas for the other substance (N-(2-Aminoethyl)-3-aminopropylmethyldimethoxysilane), it is supported by 193 out of 345 notifiers, but not by the lead registrant. Thus, most of these adhesion promoters are not classified for skin sensitization.

None of the adhesion promoters are classified for respiratory sensitization (as is MDI), but given the low vapour pressure of MDI this MDI-effect is probably not very relevant for consumer applications (generally not applying spraying for these types of products).

It should be noted that all seven adhesion promoters are classified by the main number of notifiers for eye damage (6 out of 7) or Skin Corrosion (severe skin burns). MDI is classified for skin and eye irritation and thus, in particular if used by consumers, possibly without personnel protective equipment, these severe topical effects of the alternatives should be noted.

For some of the alternatives, some notifiers have suggested classification for aquatic toxicity, just as MDI is subject to harmonised classification for this endpoint. Whether this classification might manifest in actual ecotoxicity is however questionable given the foreseen amount possibly released and the environmental fate of these alternatives (MDI e.g. is considered to immobilise in the environment).

When looking at the environmental fate parameters in Table 14, it appears that the adhesion promoters relatively quickly react with water. For one substance (3-glycidoxypropyltrimethoxysilane (Epoxy functionalised silane)), methanol is formed just like for the main monomers. Five of the others are assessed to be not readily biodegradable, but as noted for the other alternatives reviewed in this report, this appears to be logical given the polymer forming capacity.

All in all, largely based on self-classifications on the ECHA web-site, the adhesion promoters seems to differ somewhat in inherent toxicity, but in general to possess less potential for skin sensitization (although suggested classification for two of these) as compared to MDI and no/limited potential for carcinogenicity. On the other hand, and of high relevance for consumer exposure, the alternatives seem to be more aggressive in terms of eye damage and skin corrosion as compared to MDI (skin and eye irritation). Based on the available information, the alternatives seem to behave similarly to MDI in the environment.

TABLE 13
CLASSIFICATION AND LABELLING OF "OTHER HYBRID SILANE" CHEMISTRY BASED ON INFORMATION IN ECHA'S CLASSIFICATION AND LABELLING INVENTORY

CAS No.	International chemical identification (Trade name example(s))	Hazard Class and Category Code(s)	Hazard statement Code(s)	Number of notifiers
919-30-2	3-aminopropyltriethoxysilane (SiSiB® PC1100) (Geniosil® GF 93)	Acute Tox. 4 * Skin Corr. 1B	H302 H314	Not relevant (Harmonised classification)
1760-24-3	N-(2-Aminoethyl)-3-Aminopropyltrimethoxysilane (amino silane)	TOTAL		1183
		Not classified		368
	(SiSiB® PC1200)	**Skin Sens. 1**	**H317**	755
	(Geniosil® GF 9)	**Eye Dam. 1**	**H318**	693
		Acute Tox. 4	H332	260
		Aquatic Chronic 3	H412	297
		Acute Tox. 4	H302	101
		Skin Irrit. 2	H315	335
		Aquatic Chronic 2	H411	174
		Skin Corr. 1B	H314	65
		Eye Irrit. 2	H319	42
		Resp. Sens. 1	H334	9
		STOT SE 3	H335	9
		Aquatic Chronic 1	H413	1

3069-29-2	N-(2-Aminoethyl)-3-aminopropylmethyldimethoxysilane (Amino functionalised silane) (Geniosil® GF 95)	TOTAL		345
		Not classified		1
		Skin Sens. 1	H317	193
		Eye Dam. 1	**H318**	274
		Skin Corr. 1B	H314	69
		Skin Corr. 1C	H314	1
		Skin Irrit. 2	**H315**	31
		Acute Tox 4	**H302**	16
		Skin Sens. 1A	**H317**	13
		Eye Irrit. 2	H319	1
		Aquatic Chronic 3	H412	20
13822-56-5	3-Aminopropyltrimethoxysilane (Amino functionalised silane) (Geniosil® GF 96)	TOTAL		627
		Not Classified		11
		Skin Corr. 1B	H314	304
		Skin Corr. 1C	H314	1
		Eye Irrit. 2	H319	352
		Skin Irrit. 2	**H315**	210
		Eye Dam. 1	**H318**	204
		Repr. 1B	H360 (oral)	4
		STOT SE 3	H335	2

23843-64-3	3-Ureidopropyltrimethoxysilane (Amino functionalised silane) (Geniosil® GF 98)	TOTAL		351
		Not classified		22
		Skin Irrit. 2	H315	329
		Eye Dam. 1	H318	328
		Eye Irrit. 2	H319	1
		STOT SE 3	H335	65
		*no information on lead registrant		
2530-83-8	3-Glycidoxypropyltrimethoxysilane (Epoxy functionalised silane) (Geniosil® GF 80)	TOTAL		1285
		Not classified		155
		Eye Dam. 1	**H318**	496
		Skin Irrit. 2	H315	156
		Eye Irrit. 2	H319	274
		Acute Tox. 3	H331	3
		Acute Tox. 3	H301	23
		Acute Tox. 4	H302	99
		Acute Tox. 4	H312	1
		STOT SE 3	H335	21
		Asp. Tox. 1	H304	1
		Repr. 2	H316	1
		Muta. 2	H341	355
		Aquatic Chronic 2	H411	84
		Aquatic Chronic 3	H412	166

2768-02-7	Vinyltrimethoxysilane (Geniosil ® XL 10)	TOTAL		865
		Not classified		93
		Flam. Liq. 2	H225	27
		Flam. Liq. 3	**H226**	337
		Eye Dam. 1	H318	357
		Acute Tox. 4	**H332**	294
		Skin Irrit. 2	H315	190
		Eye Irrit. 2	H319	188
		STOT SE 3	H335	101
		Asp. Tox. 1	H304	32
		Muta. 1B	H340	32
		Carc. 1B	H350	32
		Carc. 2	H351	1

TABLE 14
PHYSICOCHEMICAL PROPERTIES FOR THE SEVEN ADHESION PROMOTERS BASED ON 'OTHER SILANE CHEMISTRY' IDENTIFIED IN THE PROJECT. SOURCES FOR THE INFORMATION IN THE TABLE ARE GIVEN BELOW THE TABLE

Substance	3-aminopropyltri nopropyltri-ethoxysilane	N-(3-(trimethoxysilyl)-propyl)ethylene-diamine	N-[3-(dimethoxymethylsilyl)-propyl]ethylene-diamine	3-(trimethoxysilyl)-propylamine	3-Ureidopropyltr imethoxysilane (Amino functionalised silane)	[3-(2,3-epoxypropoxy)propyl]tri methoxysilane	Trimethoxyvinylsilane
Trade name example(s)	**SiSiB® PC1100, Geniosil GF93**	**SiSiB® PC1200, Geniosil GF9**	**Geniosil GF95**	**Geniosil GF96**	**Geniosil GF98**	**Geniosil GF80**	**Geniosil XL10**
Cas no.	**919-30-2**	**1760-24-3**	**3069-29-2**	**13822-56-5**	**23843-64-3**	**2530-83-8**	**2768-02-7**
Physicochemical properties							
Physical state	Liquid[1]	Liquid[1]	Liquid[1]	Liquid[1]	Liquid[3]	Liquid[1]	Liquid[1]
Melting point (°C)	-70[2]	-38[2]	< -50[3]	< -60[1]	< -5 at 1013 hPa[3]	< -70[2]	-97[1]
Boiling point (°C)	223[1] 236 (QSAR)[1] 215[3]	140[1] 240 (QSAR)[1] 259[3]	248[*1] 110[3]	190 (QSAR)[1]	> 300 at 1013 hPa[3]	233 (QSAR)[1] 290[2]	123[1]
Relative density (g/cm^3)	0.95[1]	1.03[1]	0.98[1]	1 (QSAR)[1]	1.15[3]	1.07[1]	0.97[1]
Vapour pressure (Pa)	2[1]	0.3 - 0.4[1]	1.1 (QSAR)[1]	18 (QSAR)[1] < 500 at 50°C[3]	< 133[3]	1.1 (QSAR)[1]	1190[1] 920 (QSAR)[1]

Substance	3-aminopropyltrinopropyltri-ethoxysilane	N-(3-(trimethoxysilyl)-propyl)ethylene-diamine	N-[3-(dimethoxymethylsilyl)-propyl]ethylene-diamine	3-(trimethoxysilyl)-propylamine	3-Ureidopropyltrimethoxysilane (Amino functionalised silane)	[3-(2,3-epoxypropoxy)propyl]trimethoxysilane	Trimethoxyvinylsilane
Trade name example(s)	SiSiB® PC1100, Geniosil GF93	SiSiB® PC1200, Geniosil GF9	Geniosil GF95	Geniosil GF96	Geniosil GF98	Geniosil GF80	Geniosil XL10
Cas no.	919-30-2	1760-24-3	3069-29-2	13822-56-5	23843-64-3	2530-83-8	2768-02-7
				< 200 at 20°C[3]			
Water solubility (mg/L)	5443 (QSAR) at 20 °C[1]	> 10000 (QSAR)[1]	> 10000 (QSAR)[1]	> 10000 (read-across and QSAR) [1]	Not applicable, reacts with water[3]	> 10000 (QSAR) [1]	9400 (QSAR) at 20 °C[1] > 10000 (QSAR)[1]
Log P (octanol/water)	1.7[1] 0.31[2]	-3.4 (QSAR)[1] -0.3 (QSAR)[1]	1 (QSAR)[1] -1.4 (QSAR)[1]	-2.8 at pH 7 and 20 °C (QSAR)[1]	No information provided in SDS	-2.6 (calculation)[1] 0.5 (QSAR)[1]	-2 (QSAR)[1] 1.1 (QSAR)[1]
Environmental fate properties							
Hydrolysis /reaction with water	DT_{50}: 8.5 h at pH 7 and 24.7°C[1]	DT_{50}: 0.025h at pH 7 and 24.7°C[1]	DT_{50}: 0.25h at pH 7 at room temperatue[1]	DT_{50}: 2.6h at pH 7 at room temperature (QSAR)[1]	Reacts with water → methanol is formed)[3]	DT_{50}: 6.5h at pH 7 and 24.7°C[1]	DT_{50}: 0.2 h at pH 7 and 20°C (calculation[1] DT_{50}: <2.5 h at pH 7 and 50°C[1]
Photodegradation	DT_{50} (in air): 0.2 d at 25°C[1]	DT_{50} (in air): approx. 1 h[2]	No data[1]	No data[1]	No information provided in SDS	DT_{50} (in air): 5.8 h[2]	DT_{50} (in air): 0.372 d[2]

Substance	3-aminopropyltrinopropyltri-ethoxysilane	N-(3-(trimethoxysi-lyl)-pro-pyl)ethylene-diamine	N-[3-(dimethoxyme-thylsilyl)-pro-pyl]ethylene-diamine	3-(trimethoxysi-lyl)-propylamine	3-Ureidopropyltrimethoxysilane (Amino func-tionalised silane)	[3-(2,3-epoxypro-poxy)propyl]trimethoxysilane	Trimethoxyvi-nylsilane
Trade name exam-ple(s)	**SiSiB® PC1100, Gen-iosil GF93**	**SiSiB® PC1200, Gen-iosil GF9**	**Geniosil GF95**	**Geniosil GF96**	**Geniosil GF98**	**Geniosil GF80**	**Geniosil XL10**
Cas no.	**919-30-2**	**1760-24-3**	**3069-29-2**	**13822-56-5**	**23843-64-3**	**2530-83-8**	**2768-02-7**
	DT_{50} (in air): 2.4h[2]						
Biodegradation	Water: 67 % CO2 removal in 28 d, i.e. not readily biodegradable[1]	Water: 39 % DOC removal in 28 d, i.e. not readily biodegradable[1]	Water: Not readi-ly biodegradable (read-across)[1]	Water: Readily biode-gradable**	Readily biode-gradable[3]	Water: 37 % DOC removal in 28 d, i.e. not readily biodegradable[1]	Water: 51% O_2 consumption in 28 d, i.e. not readily biode-gradable[1]
Bioaccumulation	BCF = 3.4[1]	Waived[1]	Waived[1]	Waived as degra-dation products have low Kow[1]	BCF=3.16[4(a)]	Waived as degra-dation products have low Kow[1]	Waived as degra-dation products have low Kow[1]

* Decomposition at 248°C was observed for the substance. Pure boiling point was not observed.

**Inconsistent results from two studies, both with a reliability score of 1. One study found a degradation rate of 67% in 28 d (i.e. not readily biodegradable), the other found biodegradation of 80.2% after 28 d (readily biodegradable).

Source codes:

[1] ECHA dissemination site

[2] OECD SIDS

[3] Suppliers SDS

[4] Other information

[4(a)] http://actor.epa.gov/actor/GenericChemical?casrn=23843-64-3

3.4.3 Exposure and risk considerations for 'other hybrid silane' chemistry systems

Based on the technical data sheets for the Geniosil products identified in the current survey, the main monomers and adhesion promoters discussed in Sections 3.4.1 and 3.4.2, respectively, are typically used together, in addition to a number of further co-formulants. Example formulations from these technical data sheets are provided in Table 15. It can be seen that these systems would typically be used in adhesive and sealant applications, as also noted in Chapter 2.

TABLE 15
EXAMPLE FORMULATION TAKEN FROM THE TECHNICAL DATA SHEETS FOR THE GENIOSIL ALTERNATIVES

Main monomer	Promoters	Other co-formulants	Applications
STP-Es (10, 15, 30 or 35)	Water scavenger (e.g. Genisiol XL 10) Adhesion promoter (organofunctional silanes, possibly GF9)	Plasticizers (e.g. phthalates, polyethers) Silica Fillers (chalks, titanium dioxide) Antioxidants and UV-stabilizers	Assembly adhesives Overpaintable sealant
XB502 (Possibly together with STP-Es (10, 15, 30 or 35))	Catalysts/adhesion promoter (e.g. Geniosil GF9 Geniosil GF 95) or dioctyltin or titanium systems	Plasticizers (polyethers, phthalates, trimelletates, phosphoric acid ester) Stabilizers (stable in itself, but to achieve long time stability: various amines and oxalanilides)	Adhesives

As noted in other chapters, the nature and amount of all different ingredients in a formulation should be considered in an actual case, if MDI is substituted in a given application. E.g. attention should be paid to the amount and type of plasticizers added, which according to the examples in Table 15 could be "phthalates". That phthalates might be used as plasticizer in sealant using the 'other hybrid silane' chemistry was also found by Nilsson *et al.* (2004), see Section 3.1.3.

In relation to exposure, the main monomers as well as the adhesion promoters all have relatively low vapour pressures and thus, as a starting point, low inhalation exposure to the monomers is expected. This would also be the case if use in foam sealants in pressurized cans, if the results from the Nilsson *et al.* (2004) study are representative, see Section 3.1.3.

However, inhalation exposure might occur based on organic solvents used as propellant gases in such foam sealants. Based on Nilsson *et al.* (2004), Section 3.1.3 outlined that foam sealants might contain e.g. 'light hydrocarbons' and dimethyl ether in MDI-based foam sealants and (small amounts of) acetone, hexane and other C6-hydrocarbons in sealants based on 'other hybrid silane' chemistry. Actual use of organic solvents in such foam sealants would have to be assessed on a case-by-case basis when comparing two products and thus, no general comparison between MDI and 'other hybrid silane' chemistry based products can be made.

In addition to propellant gases, the 'other hybrid silane' based sealants split off methanol during use. Methanol is toxic via all exposure routes, including inhalation, and is clearly a point of concern for 'other hydride silane' systems if compared with MDI-based systems. Amount, rate and resulting exposure to methanol split off from these products has not been investigated in detail in the current study, although as discussed in Section 3.1.3 (based on Nilsson *et al.* (2004)), this methanol split off might cause elevated inhalation concentrations.

In relation to the skin and eye exposure routes, which are considered very likely given the possibly less frequent use of personal protective equipment among consumers as compared to professionals, MDI clearly seems to possess higher sensitizing potential than the 'other hybrid silane' systems. However, it should be noted that an EU restriction (listed in REACH Annex XVII) requires that such MDI-based consumer products should be supplied to consumers with gloves and extended safety information (see e.g. Christensen *et al.*, 2014). Such restrictions is not in place for 'other hybrid silane' systems, which inherently possess a higher potential for skin corrosion and eye damage, and further as noted already, the possibility for releasing methanol which might cause systemic toxicity following dermal exposure.

The 'other hybrid silane' systems do not seem to have a potential for (possibly) causing cancer as has MDI.

Data collected on environmental fate and effects indicate relatively low concern for MDI as well as for the 'other hybrid systems'.

All in all, these 'other hybrid silane' systems seem to possess lower severe inherent toxicity (carcinogenicity and sensibilisation), but would introduce other exposure/risk factors, including potential for releasing methanol (which might cause severe systemic toxicity following dermal contact or inhalation) and a higher potential for damage to eye and skin (eye damage and skin corrosion).

Thus, in relation to possibly substituting MDI, alternative products would thus have to be assessed case-by-case, considering:

- The degree to which methanol could be released in a given exposure scenario
- The concentration of 'other hybrid silane' monomers (affecting the potential for eye damage and skin corrosion)

- Other co-formulants (including e.g. plasticizers, where 'example formulations' in technical data sheets for 'other hybrid systems' mention phthalates as an option).

4. Conclusion

This project has aimed at identifying and assessing alternatives to MDI as monomer in adhesives, coatings and sealants for consumers. The following three groups of alternatives seem to be the most relevant from a technical and marked perspective:

- Prepolymer MDIs
- Monomers for Hybrid Non-Isocyanate-based Polyurethane (HNIPU)
- Monomers for other hybrid polymers based on silane chemistry ('other hybrid silanes')

In general, these alternatives are likely substitutes for MDI in adhesives and in particular in sealants.

Within the scope of this project, the following can be concluded for these three types of alternative systems:

Prepolymer MDIs seem to inherently possess similar toxicity as "pure"/"free" MDI and the available information on use and exposure potential does not indicate any significantly reduced risks from using these alternatives.

The **HNIPU monomers** are assessed to potentially lead to significant reduction in consumer hazards and risk.

It should however be stressed that this assessment is based on:

- Limited knowledge about the composition of the HNIPU monomers (claimed to contain "no dangerous substances" in the supplier Safety Data Sheets) and consequently, the assessment is based solely on information in the supplier Safety Data Sheets
- Limited knowledge about which co-formulants, including possible organic solvents, would be needed in addition to the HNIPU monomers for formulating adhesives, coatings and sealants.

Systems based on **monomers for 'other hybrid silane'** chemistry would typically contain: i) a 'main monomer' and ii) an 'adhesion promotor' and/or a water scavenger, in addition to other co-formulants.

All in all, these systems seem to possess lower severe inherent toxicity (carcinogenicity and sensibilisation), but would introduce other exposure/risk factors, including potential for releasing methanol (which might cause severe systemic toxicity following dermal contact or following evaporation via inhalation) and a higher potential for irritation of/effects on eye and skin (classified for eye damage and skin corrosion).

To this end, it should be noted that MDI is subject to an EU restriction requiring that gloves and extended safety information is supplied along with MDI-based products to consumers. This is not the case for 'other hybrid silane' chemistry alternatives.

In addition, phthalates might be used as plasticizers in 'other hybrid silane' based products.

None of these alternatives are considered to possess environmental fate and hazard properties significantly different than those of MDI.

Thus, in relation to possibly substituting MDI, alternative products would thus have to be assessed case-by-case, considering:

- The degree to which methanol could be released in a given exposure scenario
- The concentration of 'other hybrid silane' monomers (affecting the potential for eye damage and skin corrosion)
- Other co-formulants (including e.g. plasticizers, where 'example formulations' in technical data sheets for 'other hybrid systems' mention phthalates as an option).

Further survey and/or experimental activities on these issues would be needed to possibly being able to draw firm conclusions on MDI-based products versus products based on 'other hybrid silane' chemistry.

Thus, based on the current study, no overall conclusion can be reached for 'other hybrid silane' systems as alternatives to MDI-based systems.

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Appendix 1: Abbreviations and acronyms

ATSDR	Agency for Toxic Substances and Disease Registry
BDA	1,4-butane diamine
CEPE	European Council of the Paint, Printing Ink and Artists's Colourants
DADO	1,12-dodecane diamine
DEHP	Di(2-ethylhexyl) phthalate
DETA	diethylenetriamine
DFL	Danmarks Farve- og Limindustri – Danish Coatings and Adhesives Association
DNPH	Dinitrophenylhydrazine
DIY	Do-It-Yourself
ECHA	European Chemical Agency
EPA	Environmental Protection Agency
ESIS	European chemical Substances Information System
FEICA	Association of the European Adhesive & Sealant Industry
HDI	Hexamethylene diisocyanate
HDMI	bis(4-isocyanatocyclohexyl)methane
HMDA	1,6-hexamethylene diamine
HNIPU	Hybrid Non-Isocyanate Polyurethane
HPLC	High-performance liquid chromatography
IARC	International Agency for Research on Cancer
IPDA	isophorone diamine
IPCS	International Programme on Chemical Safety
IPDI	1-(isocyanatomethyl)-3,5,5-trimethyl-cyclohexan
ISOPA	The European Diisocyanate and Polyol producers Association
LOUS	List of Undesirable Substances (of the Danish EPA)
MDI	Methylene diphenyl diisocyanate
MS	Silyl modified Polyether
NIPU	Non Isocyanate-based Polyurethane
OECD	Organisation for Economic Co-operation and Development
OEM	Original Equipment Manufacturer
PUR	Polyurethane
SDS	Safety Data Sheet
SIDS	Screening Information Data Set
SiMP	Silyl modified polymer
SMP	Silyl modified polymer
SMX	Hybrid technology (supplied by Soudal)
STP	Silane Terminated Polymer
TDI	Toluene diisocyanate
UVCB	Substances of Unknown or Variable composition, Complex reaction products or Biological materials
WHO	World Health Organization

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Alternatives to MDI in Consumer Products

As a follow-up to the LOUS report, the current report investigates in more detail availability of alternatives to MDI in consumer products (coatings, adhesives and sealants) and assesses the health and environmental properties of these alternatives as compared to MDI.

Som opfølgning på LOUS rapporten om isocyanater, ser denne rapport på hvilke tilgængelige alternativer til MDI i forbrugerprodukter (overfladebehandlingsmidler, lime/klæbestoffer og fugemasser) der findes, samt deres miljø og sundhedseffekter i forhold til MDI holdige produkter.

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