

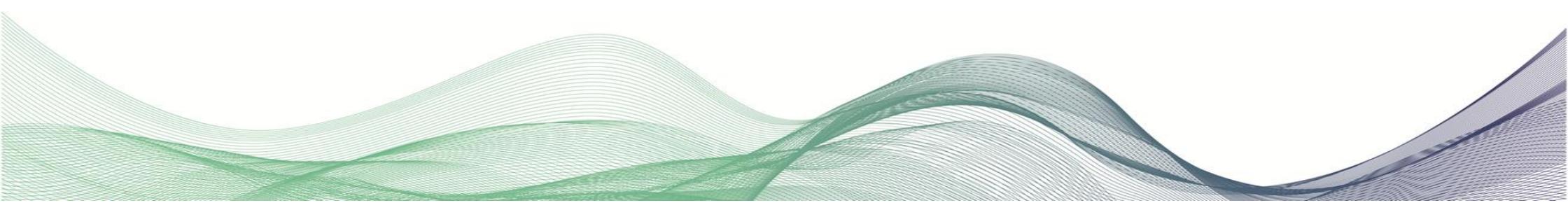
Webinar Roadmap on carcinogens Exposition in rubber industry

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Agenda

1. Manufacturing Process of rubber articles
2. Overview products & hazard analysis
3. RIE Inhalation
4. RIE Skin
5. Air sampling

1 Manufacturing process

Manufacturing process: Master Batch

Production plant foam rolls for automotive-sector

- Closed cell, semi-closed cells (needling)
- Batch Production
- Carbon black (2 kg)
- chalk (CaCO_3)
- Process oil
- Mixing process
- **Polymers** (150°C)
- Asphalt (150°C)



Manufacturing process: Final Batch

Blowing & vulcanization agents

- Added as preweights in sealed bags
 - Put on conveyor belt towards mixer
 - Rubber, preweights, asphalt, recycled material
 - Heated at 135° and 160°C
 - Cleaning agent mixers: MEK
-
- LEV not always used properly. Lots of flexible ducts and elbows → velocity losses
 - Fixed aspiration devices ? Fishtail hood?
 - Cooling zone
 - Extrusion at 40 to 80°C
 - Foamline (135 à 200°C): closed system with LEV
 - Technical failure: intervention in opened installation
 - Oven – cooling zone water - needling – cooling zone - shredder



2 Products & Hazard identification

Overview chemical agents

about 30 products with SDS

Naam	Samenstelling CAS-nr concentratie	Labels		
		H-zin	SYMBOOL	Gevaaren Klasse in-ademing
Aluminium Hydroxide Avyral 15	Aluminiumhydroxide/ 21645-51-2/ 100%	-	-	-
Aluminium Hydroxide Avyral 15 pre-weight	Aluminiumhydroxide/ 21645-51-2/ 100%	-	-	-
Asfalt- oxidized	Asfalt / 64742-93-4 / 100%	H315, H319		B
AZODICARBONAMMIDE	C,C'- azodi (formamide) / 123-77-3 / 100%	H334		D
BIK OT	-	-	-	A
Calciumcarbonaat OMYALITE 50-OM	Calciumcarbonaat / 471-34-1 / 95,00%	-	-	A
Calciumcarbonaat OMYALITE 50-OM BG	Calciumcarbonaat / 471-34-1 / 95,00%	-	-	A
Calciumcarbonaat VS 10 BG	Calciumcarbonaat / 471-34-1 / 95,00%	-	-	A
Calciumcarbonaat VS10	Calciumcarbonaat / 471-34-1 / 95,00%	-	-	A

Carbon Black	CARBON BLACK / 1333-86-4 / 100%	-	-	A
DBTU CRA	1.3-dibutylthiourem / 109-46-6 / 100%	H312, H317, H372, H401, H411		D
DPG C	1,3-difenyguanidine / 102-06-7 / 98,00% Destillaten (aardolie), met waterstof behandelde lichte paraffinehoudende / 64742-55-8 / 2,00%	H301, H315, H319, H335, H361f, H411		C
Ethyleen Propyleen Rubber KEP	Ethyleen propyleen copolymeer / 9010-79-1 / 100% Ethyleen-propyleen 5-ethyldeeen-2-norborneen terpolymeer / 25038-36-2 / 100%	-	-	A
FB POWDER 685	1.3-dibutylthiourem / 109-46-6 / 6,00% 2-mercaptobenzothiazole / 149-30-4 / 2,00% C,C'- azodi (formamide) / 123-77-3 / 63,00% Calcium silicaat / 1344-95-2 / 1,00% Destillaten (aardolie), met waterstof behandelde zware paraffine / 64742-52-5 / 1,00% Tetrabenzyl thiuram disulfide / 10591-85-2 / 2,00% Witte paraffineolie / 8042-47-5 / 1,00% Zinc bis (dibenzyl)dithiocarbonaat / 14726-36-4 / 1,00% Zwavel / 7704-34-9 / 7,00%	H317, H334, H411		D
FB POWDER 685	1.3-dibutylthiourem / 109-46-6 / 5,00% 2-mercaptobenzothiazole / 149-30-4 / 3,00% C,C'- azodi (formamide) / 123-77-3 / 62,00% Calcium silicaat / 1344-95-2 / 1,00%	H317, H334, H411		D

Perkacit ZBEC	Zinc bis (dibenzylthiocarbamaat) / 14726-36-4 / 100%	H410		A
Queo 8210	-	-	-	
RM 69 ASF	2-butoxyethanol / 111-76-2 / 8,00% Niet-ionische tensides / 69011-36-5 / 3,00% Sodium p-cumenesulphonate / 15763-76-5 / 3,00% vetalcoholalkoxylaat / 11190-53-4 / 3,00%	H315, H318		C
RUBERATOR MBT	2-mercaptobenzothiazole / 149-30-4 / 100%	H317, H410	 	C
Stearine (Radiacid) 0417	Fatty acids, C16-18/67701-03-5/100%	-		
VINYFOR AC-872	C,C'-azodi (formamide) / 123-77-3 / 75,00% Magnesium Oxide / 1309-48-4 / 12,00%	H242, H334	 	D
VINYFOR AC-872 BG	C,C'-azodi (formamide) / 123-77-3 / 75,00% Magnesium Oxide / 1309-48-4 / 12,00%	H242, H334	 	D
WD 40	Koolwaterstoffen C9-C11, n-alkanen, isoalkanen, cycloalkanen, <2% aromaten/ 919-857-5/ 70% Kooldioxide/ 124-38-9/ 2%	H222, H229, H304, H336	 	B
Zinkoxide	Zinkoxide 215-222-5/97% Loodmonoxide/1314-41-6/0.3% Cadmiumoxide/1306-19-0/1% Zinkcarbonaat/3486-35-9/1%	H400, H410		A

Hazard analysis

Main health effects

- DPG C: toxic by ingestion: CNS, liver, kidney, GI-effects
- DBTU: thyroid
- ARM69 ASF: serious eye injury
- DPG C en FB Powder EC-1200: irritation airways
- Oxidized Asphalt, DPG-C, FB Powder EC-1200, Ground sulfur oil, RM 69 ASF: skin irritation

- Sensibilization:
 - Azodicarbonamide, FB-powder EE-1000, FB Powder 685, Vinyfor AC 872: CC'-azodi (formamide)
 - DBTU CRA, FB powder 685, 1200, 1000, ruberator MBT: 1,3-dibutylthiourea + benzothiazole-2-thiol

CMR-substances

According tot sds

- DPG-C and FB Powder EC-1200 : H361f (diphenylguanidine)
- Carbon black (IARC 2B) not in SDS

Process generated carcinogens

- IARC rubber manufacturing industry: urinary tract, leukemia, lymphoma (class 1)
- Formaldehyde (upper airways)
- PAC's (skin, lung)
- Bitumen vapours

Other process generated agents

- H₂S, CO, CO₂, NH₃, Nox, SO₂, VOC
- Codex book VI, Titel 2, annex 2: nitrosamines (vulcanization and following processes of technical rubber articles and tires (stockage included), unless proved by atmospheric measurements that air concentrations of nitrosamines < 1 µg/m³.
- INRS: FAR 16 (Fiche d'aide au repérage des cancérigènes) [FAR16 \(1\).pdf](#)

3 RIE Inhalation

Results Stoffenmanager

RIE INHALATION (Stoffenmanager)

Naam/Proces	Product	Gevaarklasse inademing	Blootstelling klasse	Risicoscore	Samenstelling	RCR taak	RCR dag
Afwegen testpoeders	DBTU CRA	D	1	II	Inhaleerbaar stof	1,85	0,058
Afwegen testpoeders	DBTU CRA	D	1	II	1.3-dibutylthioureum	6,18	0,19
Afwegen testpoeders	GROUND SULFER OIL-TREATED	B	1	III	Inhaleerbaar stof	1,85	0,058
Afwegen testpoeders	GROUND SULFER OIL-TREATED	B	1	III	Destillaten (aardolie), hydrotreated heavy paraffinic, basisolie niet gespecificeerd	0	0
Afwegen testpoeders	GROUND SULFER OIL-TREATED	B	1	III	Zwavel	3,00	0,094
Afwegen testpoeders	Perkacit TBzTD pdr-d	A	1	III	Inhaleerbaar stof	1,85	0,058
Afwegen testpoeders	Perkacit TBzTD pdr-d	A	1	III	Tetrakis(phenylmethyl)thiooperoxydicarbonic diamide	1,85	0,058

RIE INHALATION

Afwegen testpoeders	Perkacit ZBEC	A	1	III	Inhaleerbaar stof	1,85	0,019
Afwegen testpoeders	Perkacit ZBEC	A	1	III	Zinc bis (dibenzylthiocarbamaat)	2,65	0,028
Afwegen testpoeders	RUBERATOR MBT	C	1	III	Inhaleerbaar stof	1,85	0,19
Afwegen testpoeders	RUBERATOR MBT	C	1	III	Benzothiazole-2-thiol	1,85	0,019
Afwegen testpoeders	BIK OT	A	1	III	Inhaleerbaar stof	1,85	0,019
Afwegen testpoeders	AZODICAR-BONAMMIDE	D	1	II	Inhaleerbaar stof	1,85	0,058
Afwegen testpoeders	AZODICAR-BONAMMIDE	D	1	II	C,C'-azodi (formamide)	3,71	0,12
Afwegen testpoeders	DPG C	C	1	III	Inhaleerbaar stof	1,85	0,019
Afwegen testpoeders	DPG C	C	1	III	1,3-difenyguanidine	6,06	0,063
Afwegen testpoeders	DPG C	C	1	III	Destillaten (aardolie), met waterstof behandelde lichte paraffinehoudende	0,074	0,0008
Afwegen testpoeders	Aluminium Hydroxide Apyral 15	A	1	III	Inhaleerbaar stof	1,85	0,019
Afwegen testpoeders	Aluminium Hydroxide Apyral 15	A	1	III	Aluminiumhydroxide	5,17	0,054
Afwegen testpoeders	VINYFOR AC-872	D	1	II	Inhaleerbaar stof	1,85	0,019

RIE INHALATION

Afwegen testpoeders	VINYFOR AC-872	D	1	II	C,C'-azodi (formamide)	2,78	0,029
Afwegen testpoeders	VINYFOR AC-872	D	1	II	Magnesium Oxide	0,22	0,0023
Afwegen testpoeders	STEARINE (RADIACID) 0417	A	1	III	Inhaleerbaar stof	1,85	0.019
Afwegen testpoeders	STEARINE (RADIACID) 0417	A	1	III	Fatty Acids, C16-18	-	-
Afwegen testpoeders	QUEO 8210	A	1	III	Inhaleerbaar stof	0,38	0,004
Afwegen testpoeders	Zinkoxide	A	1	III	Inhaleerbaar stof Zinkoxide Cadmiumoxide Loodmonoxide Zinkcarbonaat	1,85 8,99 9,27 0,37 0,1	0,019 0.094 0.097 <0.01 <0.01
Automatisch verpompen van vaste stoffen naar hopper	Calciumcarbonaat OMY-ALITE 50-OM	A	2	III	Inhaleerbaar stof	0,085	0,085
Automatisch verpompen van vaste stoffen naar hopper	Calciumcarbonaat OMY-ALITE 50-OM	A	2	III	Calciumcarbonaat	0,081	0,081

RIE INHALATION

Automatic transport (pumping) to mixer

Risk score III en RCR-score 0 of < 0,1

- Removing empty big bags of carbon black:

Lege zak-ken in con-tainer gooien	Carbon Black	A	2	III	Inhaleerbaar stof	4,24	0.018
Lege zak-ken in con-tainer gooien	Carbon Black	A	2	III	CARBON BLACK	14,14	0,059
Lossen van bigbag in afvulstation Carbon Black - kopie 1	Carbon Black	A	3	III	Inhaleerbaar stof	1,026	0.128
Lossen van bigbag in afvulstation Carbon Black - kopie 1	Carbon Black	A	3	III	CARBON BLACK	3,42	0,43

Mixing to batch

Mixen tot Batch	Asfalt-oxidized	B	1	III	Inhaleerbaar stof	0	0
Mixen tot Batch	Asfalt-oxidized	B	1	III	Asfalt	0	0
Mixen tot Batch	Aluminium Hydroxide Apyral 15 - pre-weight	A	2	III	Inhaleerbaar stof	1,87	0.117
Mixen tot Batch	Aluminium Hydroxide Apyral 15 - pre-weight	A	2	III	Aluminiumhydroxide	5,20	0,33
Mixen tot Batch	VINYFOR AC-872 - BG	D	2	II	Inhaleerbaar stof	1.868	0.117
Mixen tot Batch	VINYFOR AC-872 - BG	D	2	II	C,C'-azodi (formamide)	2,80	0,18
Mixen tot Batch	VINYFOR AC-872 - BG	D	2	II	Magnesium Oxide	0,22	0,014
Mixen tot batch	Zinkoxide	A	2	III	Inhaleerbaar stof Cadmium oxide Loodmonoxide Zink Oxide Zinkcarbonaat	1,87 9,34 0,37 9,06 0,1	0,12 0,58 0,023 0,57 <0,01
Mixen tot Batch	DPG C	C	2	II	Inhaleerbaar stof	1.868	0.117
Mixen tot Batch	DPG C	C	2	II	1,3-difenyguanidine	6,10	0,38

Mixing to batch

Mixen tot Batch	DPG C	C	2	II	Destillaten (aardolie), met waterstof behandelde lichte paraffinehoudende	0,075	0,0047
Mixen tot Batch	AZODICAR-BONAMMIDE	D	2	II	Inhaleerbaar stof	1.868	0.117
Mixen tot Batch	AZODICAR-BONAMMIDE	D	2	II	C,C'-azodi (formamide)	3,74	0,23
Mixen tot Batch	FB POWDER EE-10(17)	D	2	II	Inhaleerbaar stof	1.1868	0.117
Mixen tot Batch	FB POWDER EE-10(17)	D	2	II	Benzothiazole-2-thiol	0,037	0,0023
Mixen tot Batch	FB POWDER EE-10(17)	D	2	II	1.3-dibutylthioureum	0,31	0,019
Mixen tot Batch	FB POWDER EE-10(17)	D	2	II	C,C'-azodi (formamide)	2,58	0,16
Mixen tot Batch	FB POWDER EE-100(17)	D	2	II	Calcium silicaat	0,019	0,0012
Mixen tot Batch	FB POWDER EE-10(17)	D	2	II	Destillaten (aardolie), met waterstof behandelde zware paraffine	-	-
Mixen tot Batch	FB POWDER EE-10(17)	D	2	II	Witte paraffineolie (aardolie)	0,037	0,0023

RIE INADEMING

Mixen tot Batch	Keltan 4450S	A	1	III	Ethyleen-propylene-diene rubber	0	0
Mixen tot Batch	GROUND SULFER OIL-TREATED	B	2	III	Inhaleerbaar stof	1,868	0,117
Mixen tot Batch	GROUND SULFER OIL-TREATED	B	2	III	Destillaten (aardolie), hydrotreated heavy paraffinic; basisolie niet gespecificeerd	0	0
Mixen tot Batch	GROUND SULFER OIL-TREATED	B	2	III	Zwavel	3,02	0,19
Mixen tot Batch	DBTU CRA	D	2	II	Inhaleerbaar stof	1.868	0.117
Mixen tot Batch	DBTU CRA	D	2	II	1.3-dibutylthioureum	6,23	0,39
Mixen tot Batch	BIK OT	A	2	III	Inhaleerbaar stof	1.868	0.117
Mixen tot Batch	RUBERATOR MBT	C	2	II	Inhaleerbaar stof	1.868	0.117
Mixen tot Batch	RUBERATOR MBT	C	2	II	Benzothiazole-2-thiol	1,87	0,12
Mixen tot Batch	Perkacit ZBEC	A	2	III	Inhaleerbaar stof	1.87	0.117
Mixen tot Batch	Perkacit ZBEC	A	2	III	Zinc bis (dibenzylthiocarbamaat)	2,67	0,17
Mixen tot Batch	Perkacit TBzTD pdr-d	A	2	III	Inhaleerbaar stof	1.87	0.117
Mixen tot Batch	Perkacit TBzTD pdr-d	A	2	III	Tetrakis(phenylmethyl)thioeroxydicarbonic diamide	1,87	0,12

RIE INADEMING

Op transportband leggen van rubber	GRP BRI 75R	A	1	III	Inhaleerbaar stof	0	0
Op transportband leggen van rubber	GRP BRI 75R	A	1	III	Calciumcarbonaat	0	0
Op transportband leggen van rubber	GRP BRI 75R	A	1	III	CARBON BLACK	0	0
Op transportband leggen van rubber	GRP BRI 75R	A	1	III	Gehydrateerd aluminium silicaat	0	0
Op transportband leggen van rubber	GRP BRI 75R	A	1	III	Lubricerende olieën, C20-5-wa- terstofbehandeld neutraal gebas- seerd, hoge viscositeit	0	0
Op transportband leggen van rubber	GRP BRI 75R	A	1	III	Zink Oxide	0	0
Op transportband leggen van rubber	GRP BRI 75R	A	1	III	Zwavel	0	0

RIE Inademing

Op transportband leggen van rubber	Ethyleen Propyleen Rubber KEP	A	1	III	Ethyleen-propyleen 5-ethylideen-2-norborneen terpolymeer	-	-
Optakelen bigbags en lossen	Carbon Black	A	3	III	Inhaleerbaar stof	20,5	0,428
Optakelen bigbags en lossen	Carbon Black	A	3	III	CARBON BLACK	68,43	1,43
Plaatsen van asfalt op	Asfalt-oxidized	B	1	III	Inhaleerbaar stof	0	0
Poetsen in FB-MB	MEK TECHNICAL	B	3	II	Methylethylketon	15,24	1,90
Poetsen kalkcoater	Calciumcarbonaat OMY-ALITE 50-OM BG	A	2	III	Inhaleerbaar stof	1.045	0.131
Poetsen kalkcoater	Calciumcarbonaat OMY-ALITE 50-OM BG	A	2	III	Calciumcarbonaat	0,99	0,12
Poetsen kalkcoater	Calciumcarbonaat VS 10 BG	A	2	III	Inhaleerbaar stof	1.045	0.13
Poetsen kalkcoater	Calciumcarbonaat VS 10 BG	A	2	III	Calciumcarbonaat	0,99	0,12
Poetsen lokaal carbon black	Carbon Black	A	2	III	Inhaleerbaar stof	14.5	1.808
Poetsen lokaal carbon black	Carbon Black	A	2	III	CARBON BLACK	48,22	6,03

RIE Inademing

Poetsen lokaal carbon black - met P2	Carbon Black	A	2	III	Inhaleerbaar stof	1,447	0,181
Poetsen lokaal carbon black - met P2	Carbon Black	A	2	III	CARBON BLACK	4,82	0,60
Poetsen materialen en onderdelen machines	MEK TECHNICAL	B	2	III	Methylethylketon	1,07	0,13
Staalname procesolie	NYPAR 330	-	1	III	Destillaten (aardolie), met waterstof behandelde zware parafine	0,30	0,0093
Staalname procesolie	Paralux Proces Olie 6001R	-	1	III	Destillaten (aardolie), met waterstof behandelde zware parafine	0,30	0,0093
Storing Carbon Black installatie	Carbon Black	A	2	III	Inhaleerbaar stof	0,682	0,682
Storing Carbon Black installatie	Carbon Black	A	2	III	CARBON BLACK	2,27	2,27
Storing kalkinstallatie	Calciumcarbonaat OMY-ALITE 50-OM	A	1	III	Inhaleerbaar stof	0,214	0,214
Vervangen van filters uit filterunit Carbon black	Carbon Black	A	2	III	CARBON BLACK	2,27	2,27

Conclusion RIE Inhalation

No tasks with score I, many II & III

- **Weighing powders**: lots of tasks RCR >1, exposition 8 h < 1: foresee shielding + LEV – respiratory protection in the meanwhile, as other preweights ?
- **Automatic pumps** RCR = 0 of < 0,1 (“action level”)
- **Throwing away empty bags** chalk & carbon black: RCR > 1 → FFP3
- **Manual fill Luwipal**: Formaldehyde RCR > 1 → foresee confinement & LEV
- Unloading bigbags carbon black → FFP3
- **Unloading chalk and process oil**: RCR < 1 : OK
- **mixers**: LEV en extra confinement
- **Cleaning MEK** RCR >1; cleaning Carbon black lokal RCR > 1
- Sampling process oil RCR <1
- **Disturbances carbon black** RCR >1
- **Adding chalk to chalkcoater** RCR >1
- **Changing filters carbon black installation** RCR >1

4 RIE Skin

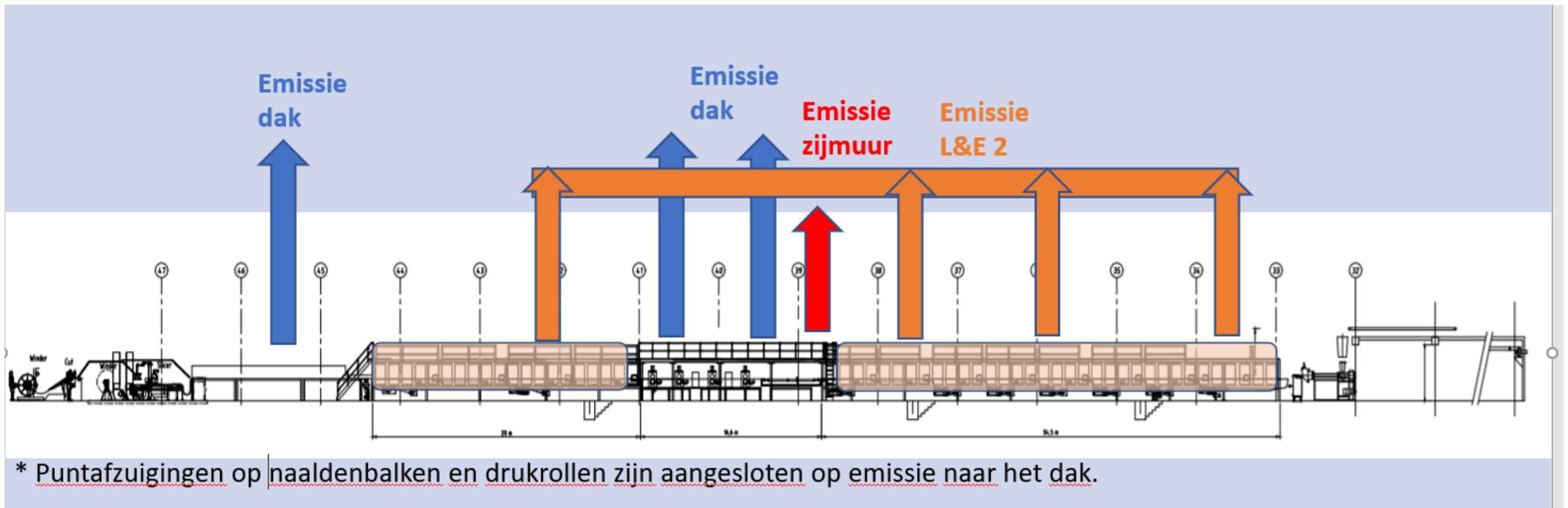
RIE HUID

Risicobeoordeling	Product	Gevaarklasse ogen	Huid lokaal: Gevaarklasse product	Huid lokaal: Blootstellingsklasse	Huid lokaal: Risicoscore	Huid opname: Gevaarklasse product	Huid opname: Blootstellingsklasse	Huid opname: Risicoscore
Afwegen testpoeders	DBTU CRA	B	D	4	I	D	4	I
Afwegen testpoeders	GROUND SULFER OIL-TREATED	C	B	4	II	-	4	III
Afwegen testpoeders	Perkacit TBzTD pdr-d	B	-	4	III	-	4	III
Afwegen testpoeders	Perkacit ZBEC	B	-	4	III	-	4	III
Afwegen testpoeders	RUBERATOR MBT	B	D	4	I	D	4	I
Afwegen testpoeders	BIK OT	B	-	4	III	-	4	III
Afwegen testpoeders	AZODICARBONAMMIDE	B	-	4	III	C	4	I

Conclusion RIE Skin

- Class danger low to medium
- Wear safety goggles (OK)
- 2 products (Ruberator en DBTU): high risk for skin
- 6 products medium risk
- Foresee gloves which chemical resistance for high and medium tasks

5 Air sampling



Measurements

Sampling plan conform NBN689:2018

- Nitrosamines: < 1 µg/m³???
 - History ? Use of other blowing agent DPT (NDEA & NDMA): research done for 2 years 2008
 - Confinement & LEV at crushing zone and rewinding zone
 - Source was blowing agent DPT
 - End of 2009: change of formula and change to Azodicarbonamide
 - Levels of nitrosamines << 0,1 µg/m³
 - Measurements 2019 en 2020 at crushing zone and exit zone oven : < 1 µg/m³
- Formaldehyde
- Carbon black
- PAK's
- Bitumen fumes
- VOC
- NH₃
- CO, CO₂, Nox, SO₂, VOC, H₂S, Azodicarbonamide

Air measurements nitrosamines

Static and Dynamic Measurements at different locations

Date	Method	Location	Value µg
21-Mar-2007	Static	Inside crushing zone cabin	40.61
28-Aug-2007	Dynamic	Compounding (mixer)	1.65
		EPT production line	7.34
		Slicers	15.34
		NVH compounding	2.27
		NVH converting	1.11
17-Oct-2007	Static	Outside crushing zone cabin	22.19
		Smoking room	11.45
		Finishing (laminators)	12.30
		End EPT production line	9.55
06-Dec-2007	Static	I-line (EC-1200, 2 nd pass)	< detection limit

2 of the 7 components were detected

- | | | |
|---|-------------|----------------------------------|
| { | NDBA | N-Nitrosodibutylamine(n) |
| | NDEA | N-Nitrosodiethylamine(n) |
| | NDMA | N-Nitrosodimethylamine(n) |
| | NDPA | N-Nitrosodipropylamine(n) |
| | NMOR | N-Nitrosomorpholine(n) |
| | NPIP | N-Nitrosopiperidine(n) |
| | NPYR | N-Nitrosopyrrolidine(n) |

CPM

Enhance LEV (less flexibles) at emission zones

Extra cameras (exit ovens) to reduce human interventions in dangerous zones

Better shielding at emission zones

Foresee general ventilation

Avoid brushing, but industrial aspirator with HEPA and squeegees

Conclusion

Titel niveau 2 Calibri Regular 20pt

- Exposition to different substances with effect of irritation or allergy
 - Exposition to different (process generated) carcinogens
 - Exposition ammonia
 - Predicted exposition MEK and carbon black above TLV
 - Weighing powders: LEV + respiratory protection
 - Mixing processes until batch
 - Optimize general and LEV
- HEPA-aspirator
FFP3, A-filter

Questions & Answers