Report **100.0015.2Q**

Bis-DMAPA-Distillation in HPI (2-step-synthesis) in Geismar
Destillationskonzept für Bis-DMAPA in der HPI (2-stufige Synthese) in Geismar

2000-02-22/Sm
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Summary
It is planned that the existing High Pressure Plant I (HPI) will produce **Bis-DMAPA** = Bis-(N,N-Dimethylaminopropyl)-amine (2-step-synthesis). **Attachment 1-3** contain the continuous distillation concept for the HPI using the columns T-1230, T-1240 and T-1250:

T-1230: system to remove ammonia into waste gas (stream 7), dimethylamine overhead (stream 5) is recycled to synthesis, T-1230 runs at 5 bar

T-1240: light ends like water, Tetra, DMAPA are separated overhead (stream 9) at 150 mbar

T-1250: pure Bis-DMAPA is produced overhead (stream 13) at 20 mbar, the heavies leave the column as bottom product (stream 12)

Because the vapor pressures of the by-product DM-DPTA and Bis-DMAPA are nearly identical, a treatment of the crude material with benzaldehyde is neccessary. DM-DPTA is eliminated by reacting with benzaldehyde to water and a heavy boiling component.
In HPI separation part a **production rate** of **21,9 t/d pure Bis-DMAPA** is possible.
The distillation concept is based on miniplant experiments at ZAT/A. **Attachment 4,5** show the experimental data for the separation of the light ends (T-1240) and **attachment 6,7** the experimental data for Bis-DMAPA purification (T-1250).
Because of identical diameters and sufficient theoretical stages the T-1240/T-1250 concept for Geismar can be transferred to **K 2400/ K 2500** in specialamine factory in Lu.
Attachment 8 shows the vapor pressures of the involved components.

Keywords multi-product-plant, distillation, Bis-DMAPA

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1. Task

The existing separation part of the High Pressure Plant I (HPI) contains the following columns

- T-1230 system to remove ammonia and recover DMA
- T-1240 system to separate light ends
- T-1250 system to produce pure Bis-DMAPA and to remove heavy ends

It is planned to produce pure Bis-DMAPA (2-step-synthesis) with a specification of > 98 weight-% containing max. 0,5 wt-% water. The present report contains a basic process proposal for the separation part of the HPI.

2. Bis-DMAPA Proposal (Attachment 1-3)

2.1 Raw Material

The concept is based on the following feed flow-rate and composition (stream 1)

Flow rate:	2 500	kg/h	
Composition:	4,5	wt.%	ammonia
	0,3	wt-%	propylamine (**PA**)
	1,9	wt-%	water
	47,0	wt.%	dimethylamine (**DMA**)
	0,5	wt.%	3-dimethylaminopropylamine (**DMAPA**)
	1,5	wt.%	N,N,N',N'-tetramethylpropandiamine (**Tetra**)
	0,9	wt%	N,N-dimethyldipropylentriamine (**DM-DPTA**)
	0,2	wt.%	3-dimethylaminopropylamin-propionitrile (**DMAPA-PN**)
	37,7	wt-%	bis-(N,N-dimethylaminopropyl)-amine (**Bis-DMAPA**)
	0,5	wt-%	N,N-bis-(3-dimethylaminopropyl)-N',N'-dimethylpropan-1,3-diamine (**Tris-DMAPA**)
	5,0	wt.%	heavies

2.2 Description

The stream from the synthesis (stream 1) contains 0,9 wt.% DM-DPTA. The separation Bis-DMAPA/DM-DPTA by distillation isn't possible because the boiling points of Bis-DMAPA and DM-DPTA differ only 0,5 °C. It is proposed to eliminate DM-DPTA by adding benzaldehyde, DM-DPTA will react to water and a heavy component.The reaction is very fast (a few minutes), so that the available residence time in T 1230 bottom is sufficient. The benzaldehyde flow-rate amounts to 20 kg/h (= 0,8 % according to stream 1).
The treated raw material (stream 3) is separated in T-1230 in ammonia via exhausted gas (stream 7), pure DMA overhead (stream 5) and light ends, Bis-DMAPA and heavies as bottom product of

T-1230. Pure DMA is recycled to synthesis. In hydramine-factory DMA-concentrations of about 99,6 wt-% (stream 5) are measured by Dr. Hunger. The reached ammonia concentration in the waste gas is unknown. The T-1230 runs at 5 bar absolute pressure.
In T-1240 the light ends like PA, water, DMAPA, Tetra are separated overhead (stream 9) at 150 mbar. Pure Bis-DMAPA is produced T-1250 overhead (stream 13). The heavies form the bottom product of T-1250. The T-1250 is operated under best vacuum = 20 mbar.

2.3 Miniplant experiments (ZAT-report 100.0021.3Q)

The distillation concept is based on miniplant experiments at ZAT/A. **Attachment 4,5** show the representative experimental data for the separation of the light ends (T-1240) and **attachment 6,7** present the experimental data for Bis-DMAPA purification (T-1250). In miniplant experiments the light ends separation runs at 100 mbar instead of 150 mbar in proposal. The higher pressure 150 mbar is proposed to facilitate the condensation in E-1241.

It is proposed that the bottom of T-1250 runs at 165 °C, because at higher temperature high boilers react increasingly back to DM-DPTA that contaminate pure Bis-DMAPA overhead. At the same time Bis-DMAPA is formed from high boilers as a positive effect. In **attachment 6,7** the measured Bis-DMAPA formation amounts to 7.1 % and the DM-DPTA formation is 268 % according to the component concentration in the feed. Because the DM-DPTA flow-rates are very low the pure Bis-DMAPA is in-spec.

2.4 Capacity

The results of the simulation show that in HPI separation part a **production rate** of **21,9 t/d pure Bis-DMAPA** is possible.

Because of identical diameters and sufficient theoretical stages the T-1240/T-1250 concept for Geismar can be transferred to **K 2400/ K 2500** in specialamine factory in Lu.

Attachment 1: Bis-DMAPA (2-step-synthesis) Separation Part

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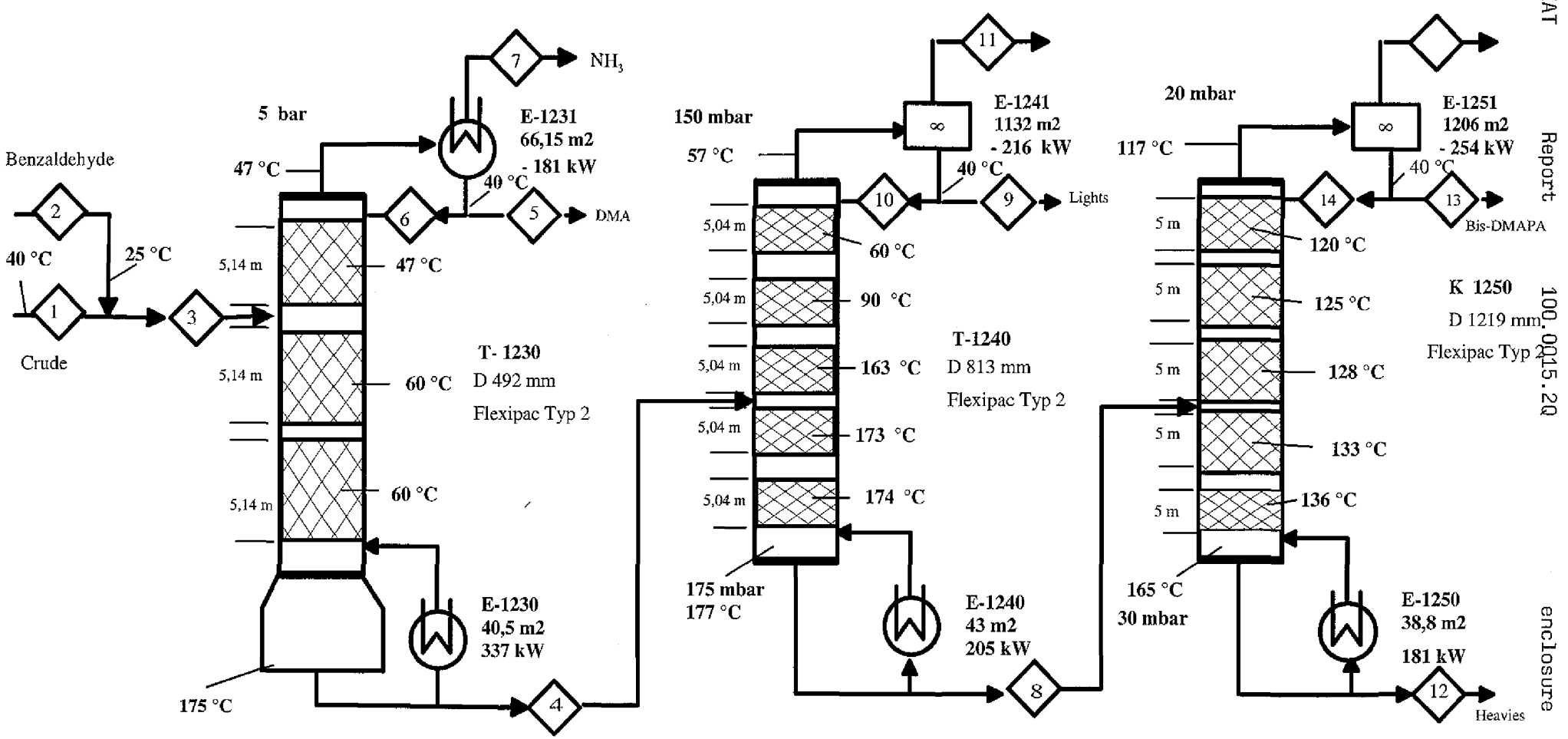
High Pressure Plant I: T-1230 / T-1240 / T-1250

7 000 t/a Bis-DMAPA



Ammonia Removal / DMA Recycle **Separation of Lights** **Bis-DMAPA Purification**

Attachment 2

Bis-DMAPA (2-step-synthesis) Separation Part

High Pressure Plant I: T-1230 / T-1240 / T-1250

7 000 t/a Bis-DMAPA

Stream		1		2		3		4	
Component	Mol-weight	kg/h	Gew-%	kg/h	Gew-%	kg/h	Gew-%	kg/h	Gew-%
Ammonia	17,03	113,7	4,5			113,7	4,5		
Proylamine	59,11	6,3	0,3			6,2	0,2	5,4	0,4
Water	18,02	47,5	1,9			49,2	2,0	49,2	4,0
Dimethylamine	45,09	1176,2	47,0			1176,2	46,7	11,1	0,9
DMAPA	102,18	12,5	0,5			12,5	0,5	12,5	1,0
Tetra	130,24	37,5	1,5			37,5	1,5	37,5	3,0
DM-DPTA	159,28	21,9	0,9			7,0	0,3	7,0	0,6
DMAPA-PN	127,23	5,0	0,2			5,0	0,2	5,0	0,4
Bis-DMAPA	187,33	941,9	37,7			941,9	37,4	941,9	75,9
Tris-DMAPA	272,48	12,5	0,5			12,5	0,5	12,5	1,0
Heavies I	250	125	5,0			125	5,0	125	10,1
Heavies II	247,38					23,1	0,9	23,1	1,9
Benzaldehyde	106,13			20	100	10,1	0,4	10,1	0,8
Total in kg/h		2 500		20		2 520		1 240,3	
Temperature in °C		40		25		40		175	

Stream		5		6		7		8	
Component	Mol-weight	kg/h	Gew-%	kg/h	Gew-%	kg/h	Gew-%	kg/h	Gew-%
Ammonia	17,03	2	0,2	0,3	0,2	111,7	95,1		
Propylamine	59,11	0,8	0,1	0,2	0,1				
Water	18,02								
Dimethylamine	45,09	1159,4	99,7	149,6	99,7	5,7	4,9		
DMAPA	102,18								
Tetra	130,24								
DM-DPTA	159,28							7,0	0,6
DMAPA-PN	127,23							5,0	0,4
Bis-DMAPA	187,33							941,8	84,5
Tris-DMAPA	272,48							12,5	1,1
Heavies I	250							125	11,2
Heavies II	247,38							23,1	2,1
Benzaldehyde	106,13								
Total in kg/h		1162,2		150		117,4		1 114,4	
Temperature in °C		40		40		40		177	

DMAPA = 3-Dimethylaminopropylamine
Tetra = N,N,N',N'-Tetramethylpropandiamine
DM-DPTA = N,N-Dimethyl-dipropylentriamine
DMAPA-PN = 3-Dimethylaminopropylamin-propionitrile
Bis-DMAPA = Bis-(N,N-Dimethylaminopropyl)-amine
Tris-DMAPA = N,N-bis-(3-dimethylamino-propyl)-N',N'-dimethylpropan-1,3-diamine

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Attachment 3

Bis-DMAPA (2-step-synthesis) Separation Part

High Pressure Plant I: T-1230 / T-1240 / T-1250

7 000 t/a Bis-DMAPA

Stream		9		10		11		12	
Component	Mol-weight	kg/h	Gew-%	kg/h	Gew-%	kg/h	Gew-%	kg/h	Gew-%
Ammonia	17,03								
Propylamine	59,11	2,9	2,5	12,7	2,5	2,5	21,2		
Water	18,02	46,8	41,0	205,2	41,0	2,4	20,0		
Dimethylamine	45,09	5,9	5,2	25,9	5,2	5,2	43,9		
DMAPA	102,18	12,4	10,9	54,5	10,9	0,1	0,5		
Tetra	130,24	36,2	31,7	158,7	31,7	1,3	11,0		
DM-DPTA	159,28		15 ppm		15 ppm			0,2	830 ppm
DMAPA-PN	127,23							5,0	2,5
Bis-DMAPA	187,33	0,1	0,1	0,5	0,1		1 ppm	35,3	17,6
Tris-DMAPA	272,48							12,5	6,2
Heavies I	250							125	62,2
Heavies II	247,38							23,1	11,5
Benzaldehyde	106,13	9,7	8,5	42,5	8,5	0,4	3,3		
Total in kg/h		114,1		500		11,9		201,1	
Temperature in °C		40		40		40		175	

Stream		13		14					
Component	Mol-weight	kg/h	Gew-%	kg/h	Gew-%	kg/h	Gew-%	kg/h	Gew-%
Ammonia	17,03								
Propylamine	59,11								
Water	18,02		< 0,5		< 0,5				
Dimethylamine	45,09								
DMAPA	102,18								
Tetra	130,24								
DM-DPTA	159,28	6,8	< 1,5	7,5	< 1,5				
DMAPA-PN	127,23								
Bis-DMAPA	187,33	906,5	> 98	992,5	> 98				
Tris-DMAPA	272,48								
Heavies I	250								
Heavies II	247,38								
Benzaldehyde	106,13								
Total in kg/h		913,3		1 000					
Temperature in °C		40		40					

DMAPA = 3-Dimethylaminopropylamine
Tetra = N,N,N',N'-Tetramethylpropandiamine
DM-DPTA = N,N-Dimethyl-dipropylentriamine
DMAPA-PN = 3-Dimethylaminopropylamin-propionitrile
Bis-DMAPA = Bis-(N,N-Dimethylaminopropyl)-amine
Tris-DMAPA = N,N-bis-(3-dimethylamino-propyl)-N',N'-dimethylpropan-1,3-diamine

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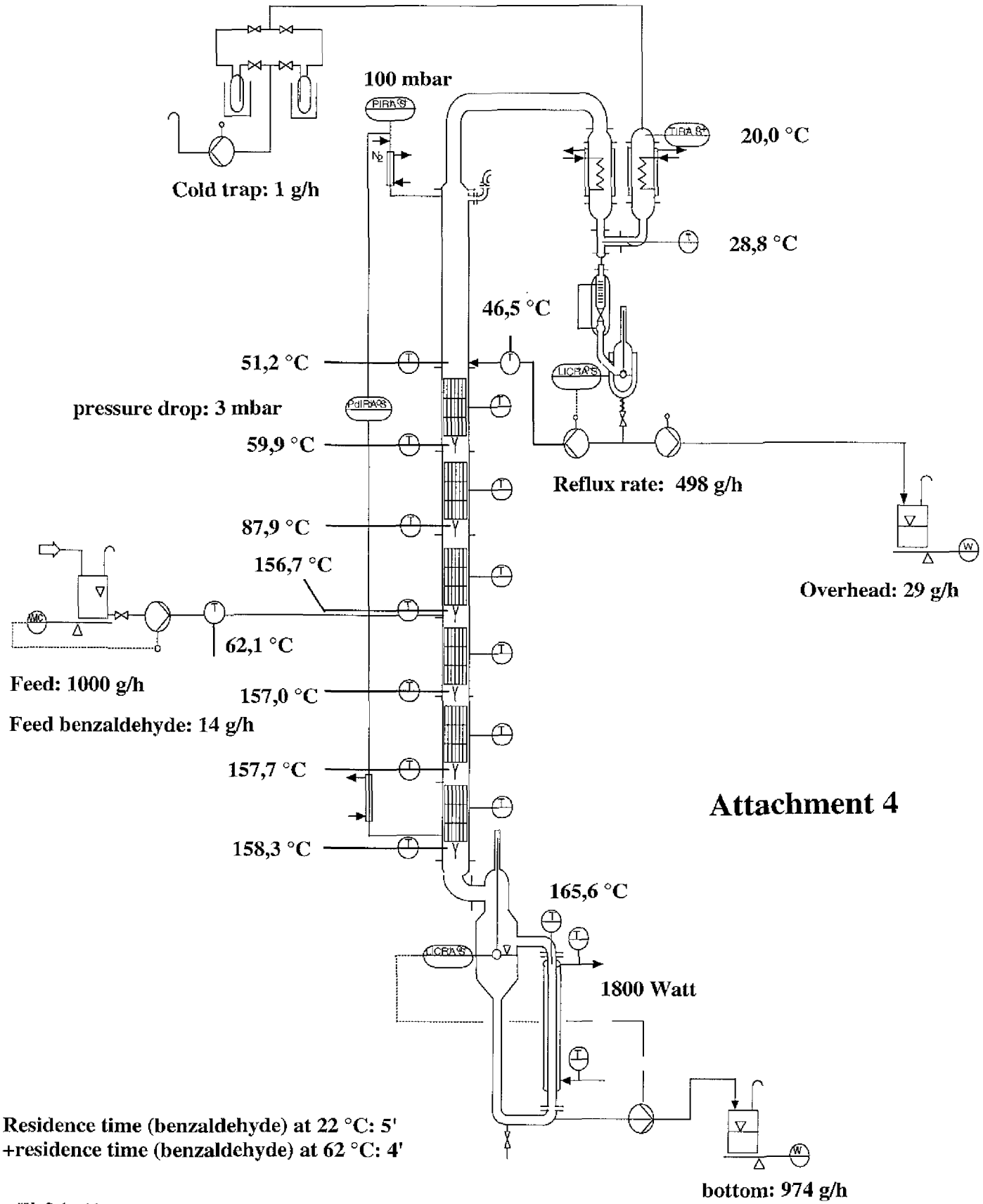

Attachment 4

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Part of ZAT-Report 100.0021.3Q

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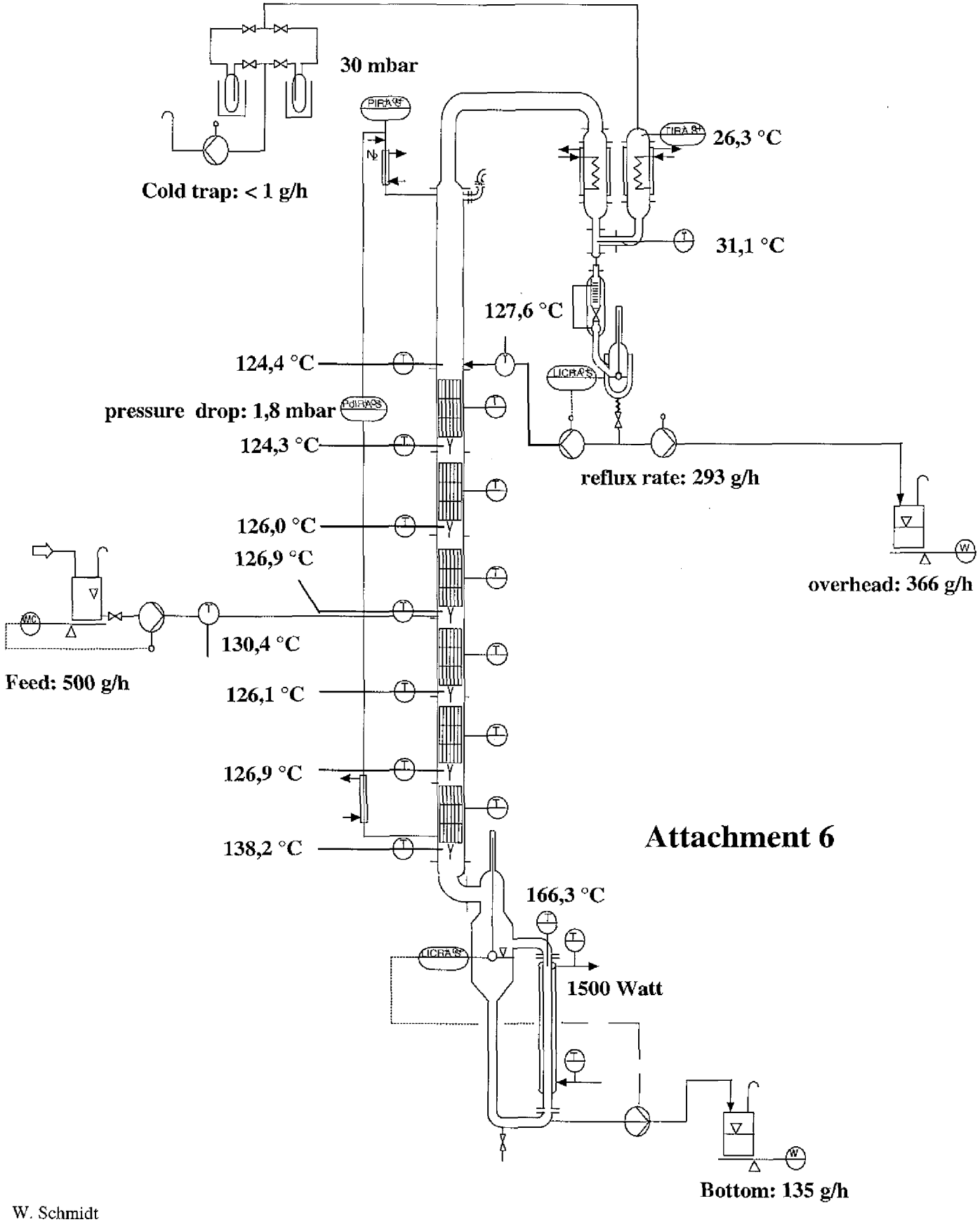
BASF

Bis-DMAPA (2-step-synthesis) Separation of Light Ends

Experiment 5: 1./2.2.2000, 16.00 – 7.30



Attachment 6

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Part of ZAT-Report 100.0021.3Q

BASF

Bis-DMAPA (2-step-synthesis) Purification
Experiment 10: 11./12.2.2000, 15.00 – 9.00

Bis-DMAPA (2-step-synthesis) Purification

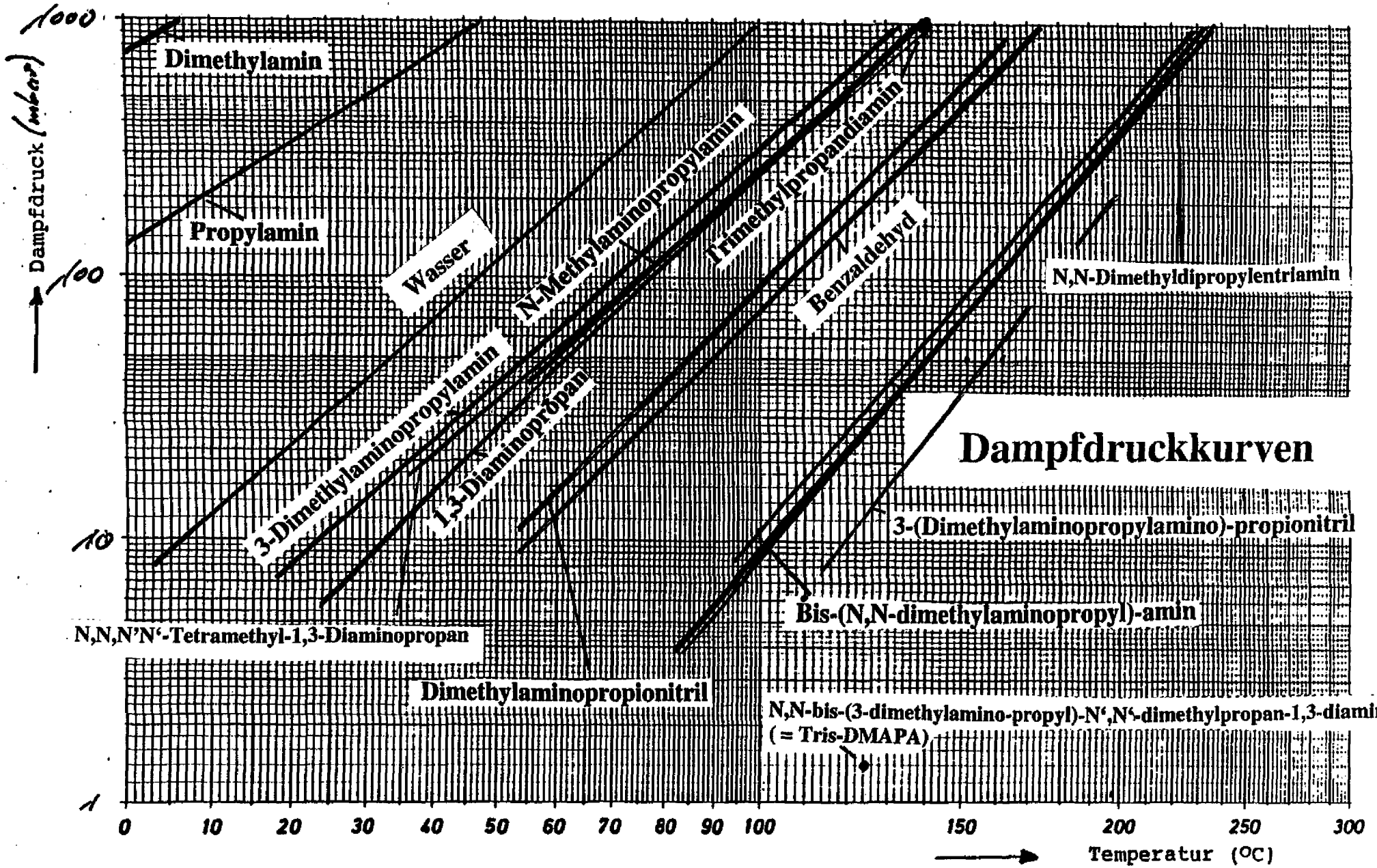
Experiment 10: 11./12.2.00, 15.00-9.00

Analysis: CZA/V; Water in wt-%; all other components in Fl-%

		Feed 12.2.2000, 9.00	Bottom 12.2.2000, 9.00	Overhead 12.2.2000, 9.00	Cold trap no sample
Water		0,14	0,09	0,13	-
DMA	RT 2,15	0,02	0,04	0,03	-
PA		-	-	-	-
DM-PA	RT 2,25	-	-	-	-
DMAPA	RT 2,7	0,11	0,02	0,54	-
DM-PDA	RT 2,81	-	-	-	-
TriMe-PDA		-	-	-	-
DMAPN		-	-	-	-
TetraMe-PDA	RT 2,93	-	-	-	-
Benzaldehyd	RT 3,3	-	-		-
DM-P-PDA	RT 3,85	-	-	-	-
	RT 5,44	-	-	-	-
DM-DPTA	RT 6,3	0,19	0,24	0,87	-
TriMe-DPTA	RT 6,60	-	-	-	-
DMAPA-PN	RT 6,85	-	-	-	-
Bis-DMAPA	RT 7,12	70,62	13,97	98,37	-
	RT 11,30	0,1	0,1	-	-
TrisDMAPA	RT 11,60	4,81	15,07	-	-
	RT 12,25	0,61	1,41	-	-
DM-DPTA+BA	RT 14,4	4,06	7,98	-	-
	RT 16,15	0,13	0,14	-	-
	RT 16,30	7,67	12,08	-	-
	RT 17,0	2,51	5,04	-	-
	RT 19,4	0,75	2,26	-	-
	RT 20,6	0,64	1,40	-	-
	RT 27,5	0,56	1,97	-	-
	RT 27,8	1,38	2,9	-	-
	RT 68,6	-	-	-	-
Others		5,7	35,31	0,06	-

DMA	**Dimethylamin**	**PA**	**Propylamin**	**DM-PA**	**Dimethylpropylamin**
1,3-DAP	**1,3-Diaminopropan**	**MAPA**	**Methylaminopropylamin**	**DM-DPTA + BA**	**Reaktionsprodukt mit Benzaldehyd**
DMAPA	**3-Dimethylaminopropylamin**	**DM-PDA**	**N,N'-Dimethyl-propandiamin**		
TriMe-PDA	**N,N,N'-Trimethyl-propandiamin**	**DMAPN**	**Dimethylaminopropionitril**		
TetraMe-PDA	**N,N,N',N'-Tetramethyl-propandiamin**	**DM-P-PDA**	**N,N-Dimethyl-N'-propyl-propandiamin**		
DM-DPTA	**N,N-Dimethyl-dipropylentriamin**	**TriMe-DPTA**	**N,N,N''-Trimethyl-dipropylentriamin**		
DMAPA-PN	**3-Dimethylaminopropylamin-propionitril**	**Bis-DMAPA**	**Bis-(N,N-Dimethylaminopropyl) amin**		

Attachment 7



25.11.99
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Attachment 8