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REPORT

UNIDO PROJECT MP/CPR/99/175

WORKSHOP

System House services for formulation of CFC-free Polyurethane Foams

Institute for Polyurethane Technology

Hamburg
October 2000

INPUT Institute for Polyurethane Technology - Hamburg

Workshop in China

Report

The workshop took place in Yantai, P. R. China, at the Marina Hotel from September, 9th to September, 10th, 2000

Participants:

Wanhua Company:	Qu Jin Sheng, General Manager
	Yu Jiang, Reception Section Chief
	Qu Wen Xiang, Routine Vice-General Manager
	Sheng Xiaolan, Interpreter
	Tian Hong Yan, Technician
	Further Technicians
SEPA:	Ma Qi, Director
	Chen Zhi Jie, Senior Engineer
	Tang Boming, Project Officer
	Chen Yang, Project Officer
	Fu Yongbin, Project Officer
China Plastic PIA:	Liao Zhengpin, Senior Engineer
UNIDO Consultants:	Kai Klockemann, Marketing and Economics
	Dr. Sven Uwe Keimling, Technician
	Dr. Jürgen Rothe, Technician

Workshop day 1, September 9th

At the beginning of the workshop we received an agenda written in Chinese, and a feasibility study written in English, performed by BCEL. The morning was used for several speeches of Wanhua and SEPA responsibles given in Chinese language and translated by the Wanhua interpreter. After that Mr. Weng Heping gave an introduction of PU rigid foams in China. He mentioned that PU started in China in 1964 with flexible foams. Nowadays all kinds of PU material were produced such as integral skin and rigid foams. The rigid foam market was divided in insulation for pipes, buildings and trucks as well as in foams for refrigerators, which today would be a total system house business. The main blowing agent used by small and medium sized enterprises was still CFC 11. The only considered replacement is HCFC 141b, which makes necessary adjustments on the existing formulations. Besides the foam production China produces raw materials like polyols, isocyanates and additives by itself. The domestic raw material supply is growing and the quality is close to foreign products.

Thereafter the representative of BCEL also gave a short explanation of their feasibility study. He pointed out that Wanhua were the largest company in this market segment, having experience in rigid polyurethanes and production of isocyanates as well as special polyol types. Because of free capacity the additional demand through the sytem house would not affect the existing production. 50 % of the potential customers of the planned system house are located in a 300 km radius around Yantai. The transportation of the blended system shall be conducted with trucks. The delivery of raw materials to the system house can be carried out either by trucks or trains as well as with ships since the Yantai harbour is only 1.5 km away.

Referring to the representatives's exposition we gave the following remarks and questions:

- The basis for the storage and blending unit is a formulation which employs three different polyether polyols (named 403, 410 and 450), one silicone surfactant, one catalyst, flame retardant, water and blowing agent (HCFC 141b). Especially the limited number of additives (surfactant, catalyst) does not enable a flexible processing. Modern formulation, in particular if used for different applications, requires e.g. more than one catalyst and blowing agent. Thus a preblending unit / reactor should be established, providing the possibility to prepare additive preblends.

- We enquired the viscosity working range of tubes and pumps. According to their answer they are capable to meter low viscous as well as high viscous products.
- Cleaning of tanks and reactors.

Our questions were answered very concisely and no deeper discussion could be started.

Our presentation consisted of an overview about the development and changes of the polyurethane industry in the last 10 years since the phase-out of CFCs in Europe and the United States. The subjects of our presentation were as follows:

- Basic reactions which take place during the polyurethane formation.
- Types of isocyanates.
- Types and manufacturing of polyether and polyester polyols.
- Influence of polyol types on physical foam properties.
- Application of catalysts to promote various PU reactions. Difference between gelling and blowing catalysts and their impact on foam properties.
- Major functions of silicone surfactants.
- Purpose of the use of blowing agents.
- Types of flame retardants.
- Introduction of test methods for raw materials and final products.
- Introduction of laboratory equipment to fulfil the test method standards.
- Presentation of PC® REX, a computer software for formulating and managing of polyurethane and epoxy systems with examples.

Workshop day 2, September 10th

In the morning visit of the Wanhua Group Company and their MDI plant. The existing system house was shown with its blending unit and two older dispensing units. The first, a low-pressure type manufactured in the former German Democratic Republic, was out of use. The other one is a two-line, high-pressure machine from Cannon, used for testing and developing of their formulations employing various moulds.

Thereafter resumption of the discussion the day before. Main subject was the feasibility study. The heat-exchanger of the blending vessel (inside and outside installation) seemed in our opinion overdone, since no exothermic reaction takes place during the blending. We were told that these heat-exchangers were needed to overcome the seasonal temperature differences (cold winter, hot summer). Nevertheless, these marginal temperature problem can be solved by the installation of a simple heat-exchanger and the use of preheating devices for higher viscous materials.

One subject, which was not mentioned in the feasibility study was the schedule for developing a CFC free system. It was claimed that CFC free formulations are already available and that there is no necessity to develop new ones. Unfortunately they did not expose these formulations as a basis for a detailed discussion. In addition, based on the kind and quality of the questions asked by the participants and the very poor response in discussion, we had the impression that external expertise is still mandatory for successfully setting up and running the planned system house.

As a further alternative blowing agent besides CFC 11 we introduced pentane, which is well established in Europe and also used in China by various system houses. The known incompatibility of pentanes with polar components such as polyols could be overcome by applying special additives. We showed some samples of poylol / pentane blends. One of them was the normal cloudy emulsion, whilst the other ones were clear solutions of polyol and pentane by using special types of silicone surfactants. They were however not interested in that and mentioned that this project is strictly bound to the use of HCFC 141b.

Conclusion

The Wanhua company is certainly capable to run a system house for CFC free rigid polyurethane formulations. Their location include all logistic possibilities such as tranportation with trucks, trains and ships and they have the isocyanate (MDI) on site. However, several items in their feasibility study should be revised. The flexibility of the system house with respect to storage and processing capability has to be increased. Storage capacity for various catalysts, surfactants and blowing agents should be considered as well as the possibility to produce and store preblends, e.g. catalyst systems. The use of polyester polyols instead of polyether polyols should also be taken into account, due to price effectivness and better flame retardancy. For this reason pumps and tubes must be designed for a wider viscosity range, especially in winter time. A preheating unit should be installed for an easier handling of higher viscous products. The design of the reactor, in particular the heat exchanger, should be revised, since no exothermic reaction takes place which requires such an intense heat exchanging.

Furthermore, the estimated costs for establishing a system house at the Wanhua company are noticeably too high. Considering local machine part manufacturer for reactors, pumps, tubes and a reasonable design for the blending unit only a fraction of the expenses are needed.

Besides that, HCFC 141b is just an interim solution and its phase-out is already scheduled. Apart from short-term planning, other alternative blowing agents such as pentane should absolutely be part of a system house concept. It is a fact, that on one hand HCFC 141b must be replaced in the future and on the other hand HCFC 141b is not suitable for all kind of application. As a result, the technology of using pentane as blowing agent is already known in several Chinese system houses, saving future investments by providing a long-term solution.

Enclosures

- General information on polyurethane (presentation)
- Standard test methods (presentation)

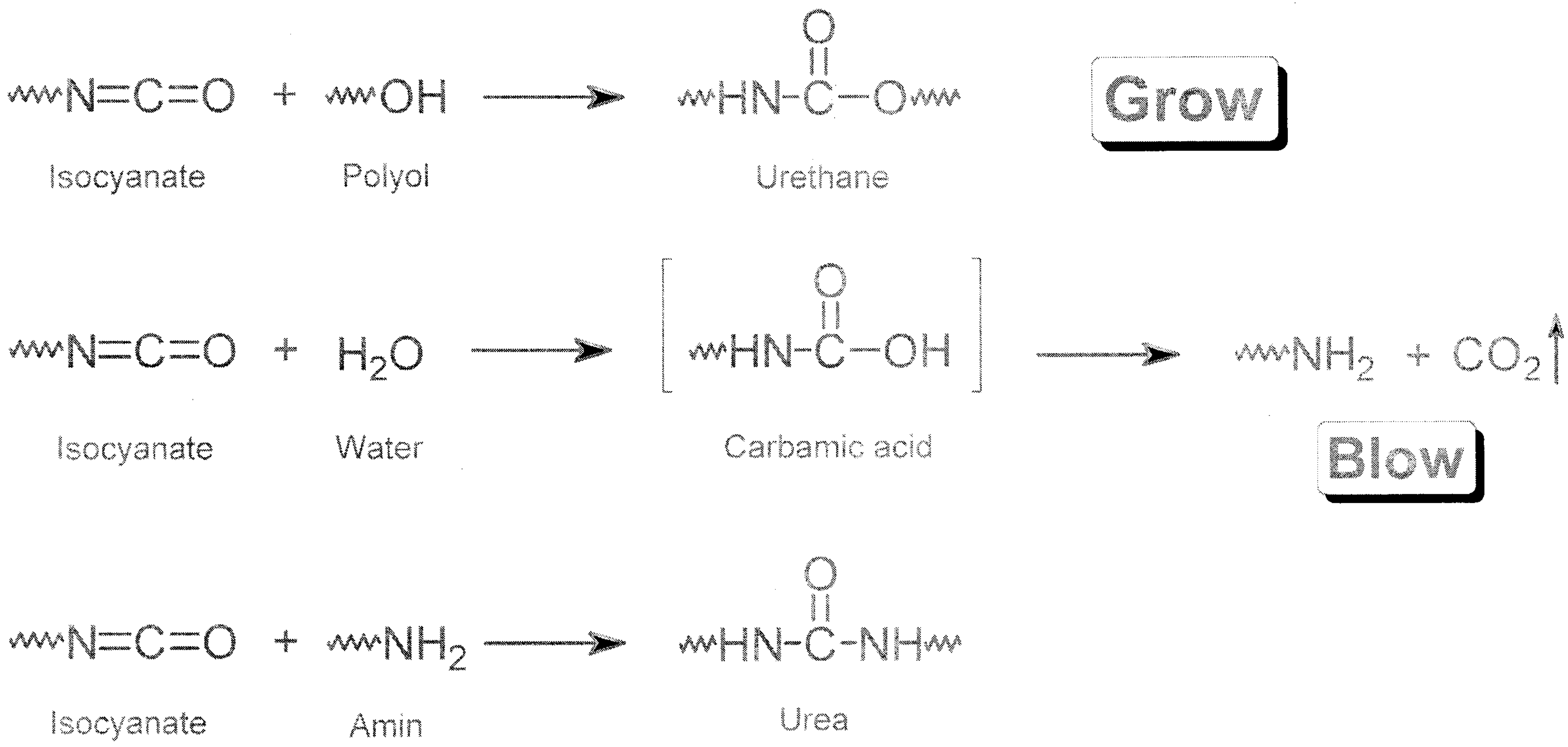
Polyurethane - Workshop

Establishment of a System House for CFC-free PU Foam Production

Yan Tai, 9 – 10 September 9th, 2000

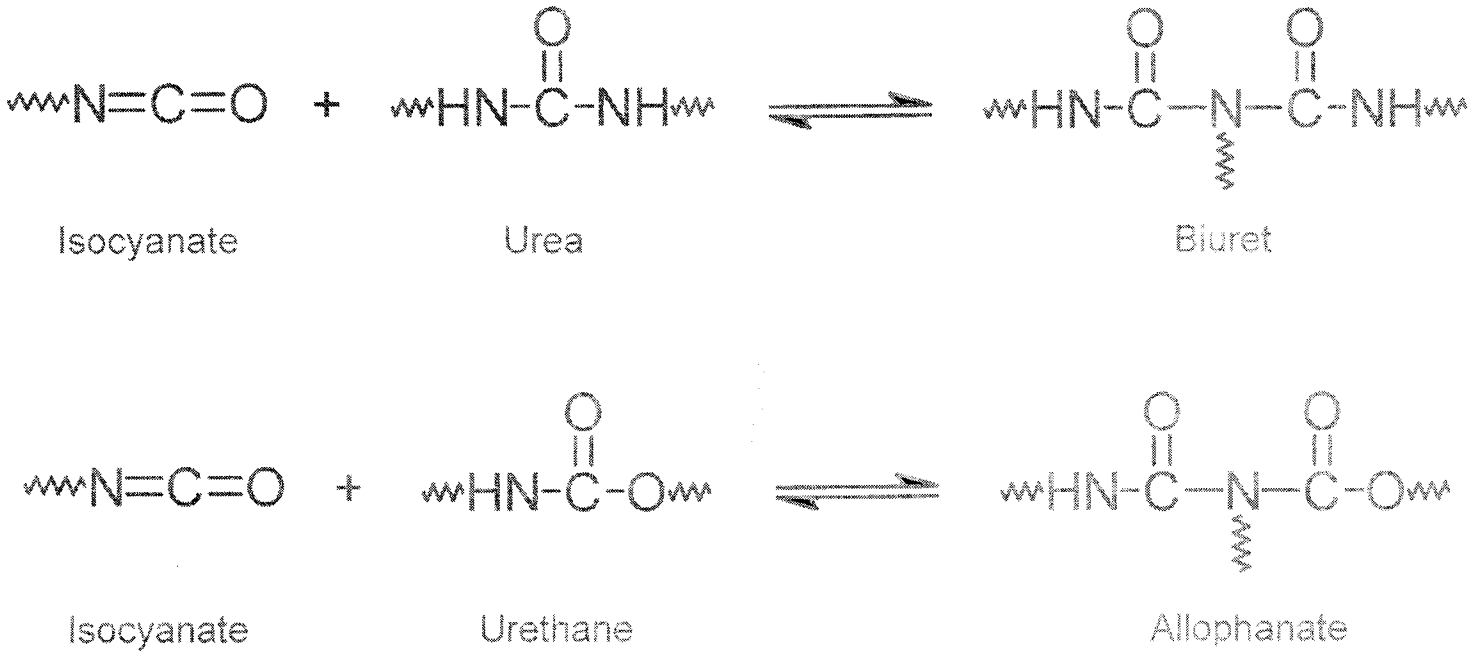
INPUT Institute for Polyurethane Technology

PU Foam reactions (1)



PU Foam reactions (2)

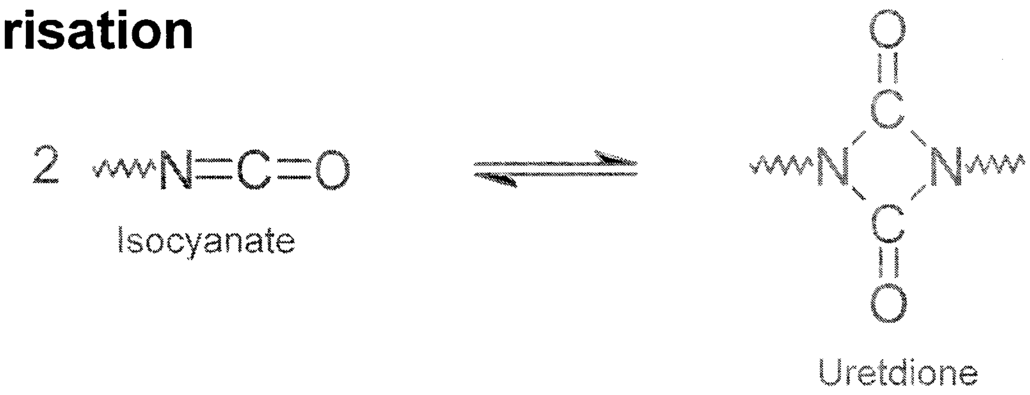
(Crosslinking)

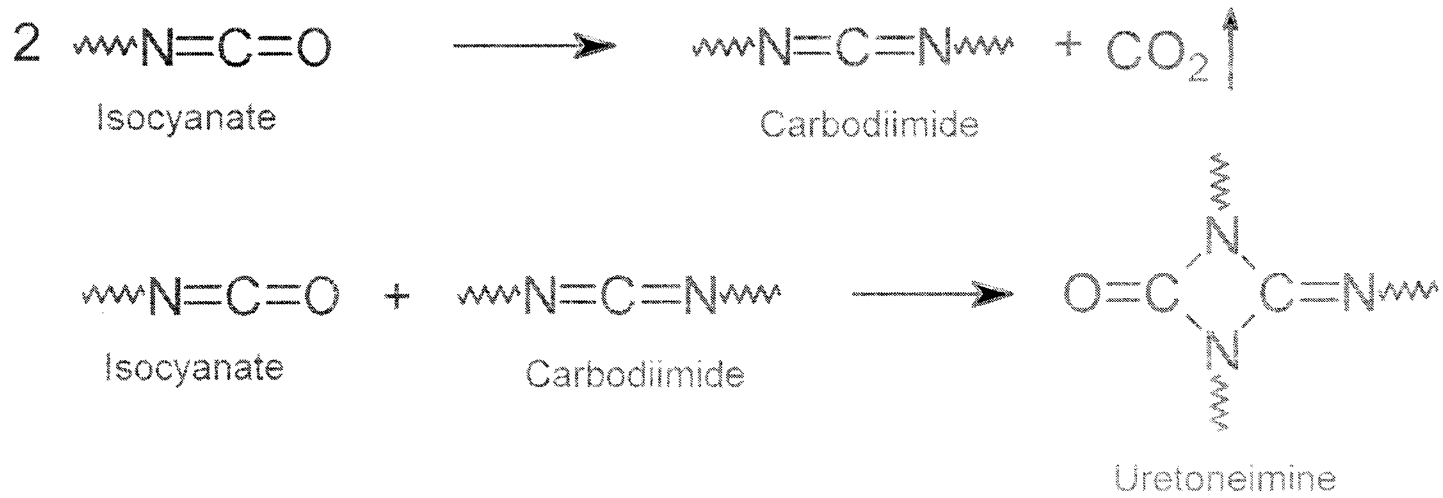


Institute for Polyurethane Technology

Oligomerisation reaction of isocyanates

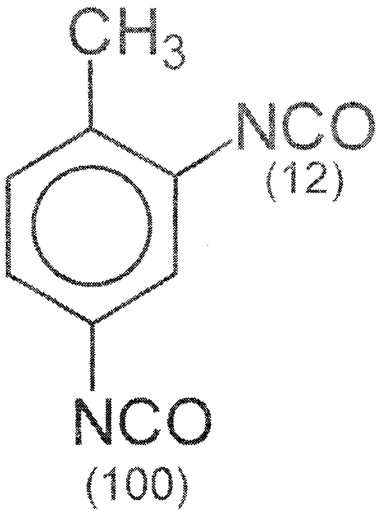
Dimerisation

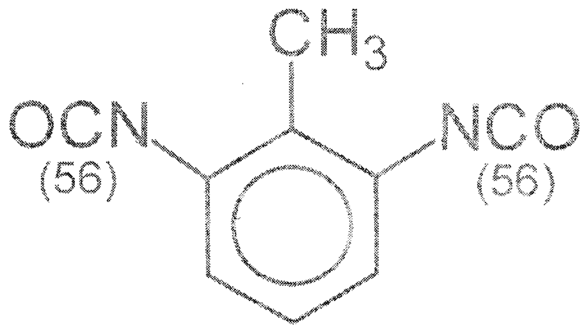




AROMATIC ISOCYANATES

Toluenediisocyanates (TDI)



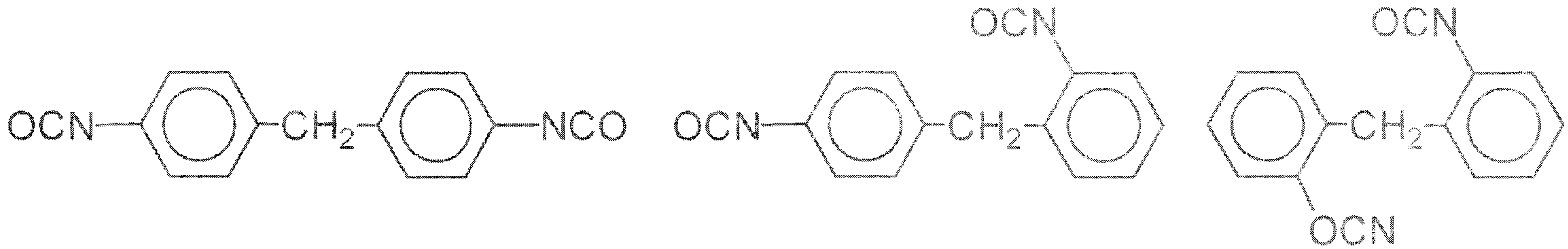


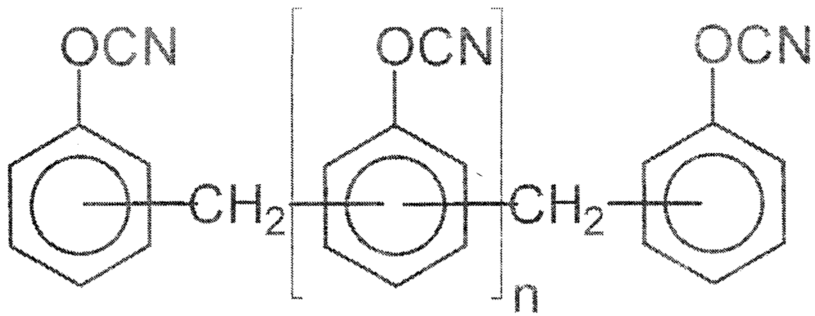
TDI 65/35: Mixture of 65% of 2,4 isomer and 35% 2,6 isomer

TDI 80/20: Mixture of 80% of 2,4 isomer and 20% 2,6 isomer

AROMATIC ISOCYANATES

Diisocyanatodiphenylmethane (MDI)





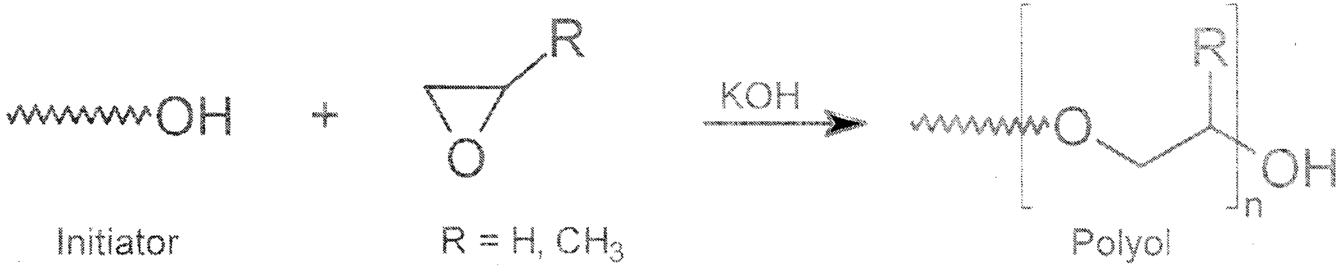
Polymeric MDI

Dinuclear component: 30 – 70%
Trinuclear component: 15 – 40%
Higher nuclear comp.: 15 – 30%

Viscosity: 50 – 200,000 mPas
NCO content: 25 – 33%

POLYETHER POLYOLS

General production



Physical properties of the polyols derives from

- **type of initiator**
- **EO/PO ratio**
- **molecular weight**
- **primary hydroxyl content**

POLYOL TYPES

Polyether polyols

Type	I	II	III	IV	V	VI
Initiator	Glycol	Trimethylol-propane	Trimethylol-propane	Saccharose, Glycol	Amin	Glycerol
Functionality	2	3	3	8	4	3
Chain extender	PO	EO/PO	EO	PO	PO	PO
av. mol. weight	2000	4800	440	860	3750	3000
Appearance	Clear, Colourless	Clear, Colourless	Clear, Colourless	Clear, yellow - brown	Clear, Colourless	Clear, Colourless
Hydroxyl number [mg KOH/g]	56	35	380	380	60	56
Viscosity @ 25°C [mPas]	250 - 350	750 - 900	600 - 700	11000 - 15000	580 - 720	450 - 550

POLYESTER POLYOLS

General production

Alcohol   Carbonic acid   Polyester

Physical properties of the polyols derives from

- type of alcohol
- type of carbonic acid
- molecular weight distribution

POLYOL TYPES

Polyester polyols

Type	I	II	III	IV	VI
Initiators	Adipic acid, glycol	Adipic acid, glycol, TMP	Adipic acid, phthalic anhydrid, ethylene glycol	Adipic acid, phthalic anhydrid, isophthalic acid, hexanediol, TMP	Hexanediol, poly-carbonate
Functionality	2	2.53	2	~3	2
av. mol. weight	2000	2370	1750	~1200	2000
Hydroxyl number [mg KOH/g]	56	60	64	140 - 150	56
Viscosity @ 75°C [mPas]	500 - 600	925 - 1075	2200 - 3140	2200 - 3140	2300

POLYOL TYPES

Impact of aliphatic/aromatic polyols on foam properties

Foam Properties	aliphatic — aromatic
Flame retardancy	
Insulation	
Dimensional Stability	
Processability	

In addition nitrogen containing aliphatic polyols enhance flame retardancy and improve the insulation.

ADDITIVES - Catalysts

Velocity of typical PU reactions

No.	NCO type	Reaction partner	Product	Rel. Speed at 30°C
1	aromatic	alcohol	urethane	moderate
2	aromatic	water	amine and CO_2	moderate
3	aromatic	amine	urea	fast
4	aromatic	urea	biuret	slow
5	aromatic	urethane	allophanate	very slow

ADDITIVES - Catalysts

Suitable chemicals as PU catalysts

No.	NCO type	Reaction partner	Catalysts
1	aliph./arom.	alcohol	tertiary amines, organometallics, metal salts
2	aliph./arom.	water	tertiary amines, organometallics
3	aliph./arom.	urea	not necessary
4	aliph./arom.	urethane	metal salts
5	aliph./arom.	dimerisation	organic phosphorous compounds, imidazoles
6	aliph./arom.	trimerisation	strong bases, metal salts, tertiary amines

ADDITIVES - Catalysts

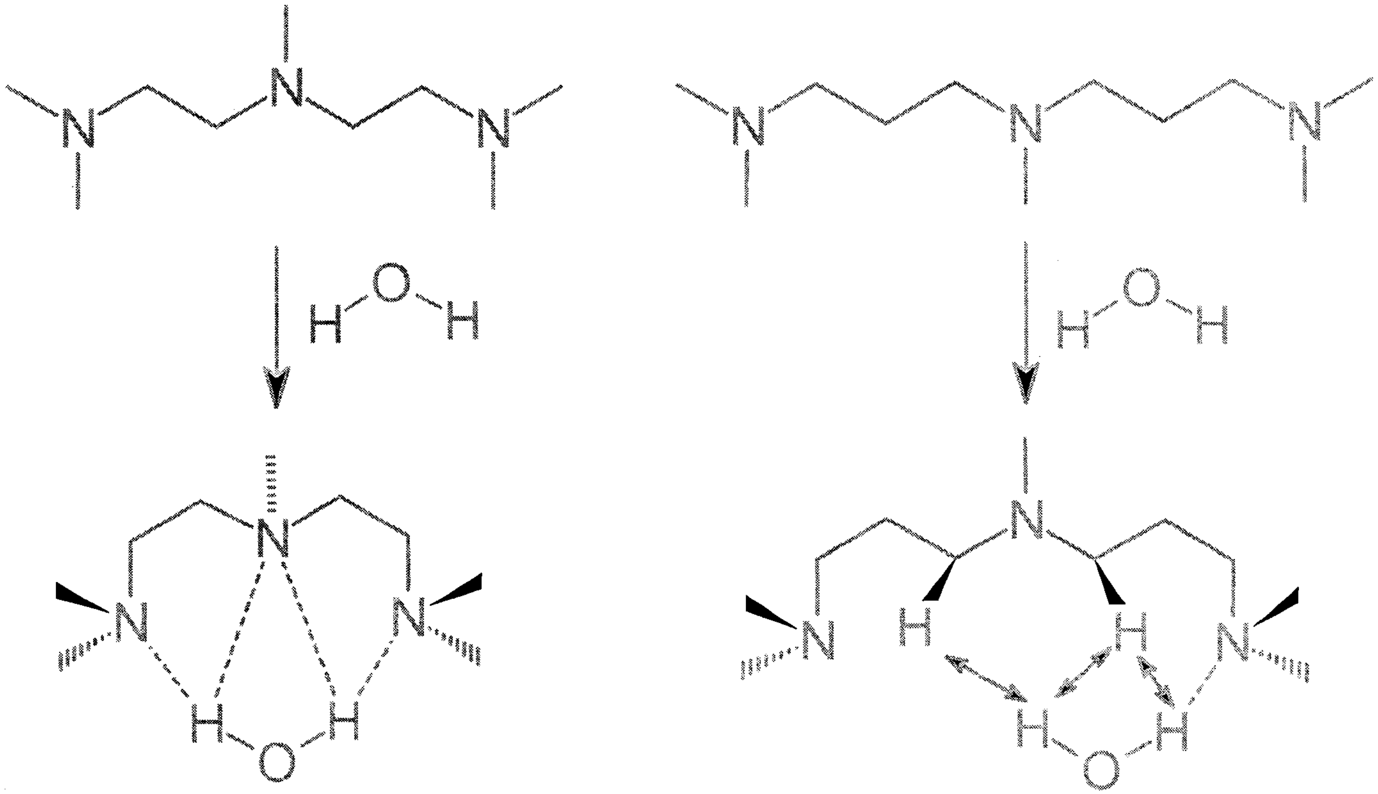
Definition of „Gel“ and „Blow“ Catalyst

Gelling catalyst: Promotes mainly the polyol isocyanate reaction

Blowing catalyst: Promotes mainly the polyol water reaction

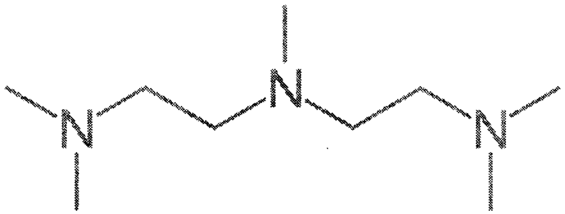
ADDITIVES - Catalysts

Difference of „Gel“ and „Blow“ Catalyst



ADDITIVES - Catalysts

Difference of „Gel“ and „Blow“ Catalyst



PMDETA

PMDPTA

Catalyst	Gelling activity	Blowing activity	Ratio (Blow / Gel)
PMDETA	4.26	15.90	37.3
PMDPTA	3.80	1.16	3.05

ADDITIVES - Catalysts

Impact of Gel – Blow Selectivity

Catalyst properties	strong blow strong gel
Flowability	
Isotropy	
Dimensional Stability	
Density	
Friability	
PIR yield	
Carbodiimid	
PUR cure	
PIR cure	

ADDITIVES – Surfactants

Major functions:

- To lower of the surface tension
- To improve the miscibility of the reaction ingredients
- To enable air to be beaten into the mixture
- To stabilise the foam bubbles
- To reduce the size of the bubbles
- To prevent coalescene of bubbles

ADDITIVES – Surfactants

Types of surfactants

- The mainly applied surfactants are polyethermodified polysiloxanes.
- The siloxane backbone (non-polar) lowers the surface tension.
- The polyether chain (polar) is responsible for the emulsification effect.
- Structurally correspond to various linear or branched head/tail configurations
- Attachment of polyether chain to the siloxane backbone:

via Si-O-C bond	hydrolysable
via Si-C bond	non-hydrolysable

ADDITIVES – Surfactants

	Si units	Si/PE ratio	% EO	Mol. Weight PE
Rigid foam	10 – 50	3/1 – 10/1	> 50	400 – 1500
Flexible foam	30 – 150	5/1 – 15/1	50	2500
HR flexible foam	< 20	3/1 – 8/1	0 – 100	200 – 1000
Polyester foam	10 – 20	2/1 – 1/1	> 70	200 - 1000

ADDITIVES – Surfactants

The HLB scale (*H*ydrophilic-*L*ipophilic-*B*alance)

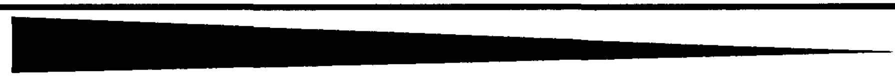
- Scale from 0 – 20 describes polarity of surfactants
- Lipophilic surfactants have low HLBs (3 – 6) → low water solubility.
- Hydrophilic surfactants have high HLBs (8 – 18) → high water solubility.
- In the middle (10 – 16) there are very surface active compounds such as silicone surfactants for PU.
- The HLB value is calculated for nonionic surfactants as follows:

$$HLB = mol\%\ hydrophilic\ group / 5$$

- Hydrophilic group = EO content for PU surfactants.
- A more precise HLB number considers also the polarity of other groups.

ADDITIVES - Surfactants

Impact of surfactant polarity

Surfactant polarity	High HLB Low HLB
Cell size	
Isotropy	
Thermal conductivity	
Dimensional Stability	
Density	
Flowability	
Distribution flow	
Compression strength	

BLOWING AGENTS

Purpose of use

- Reduction of foam density
- Reduction of the exotherm

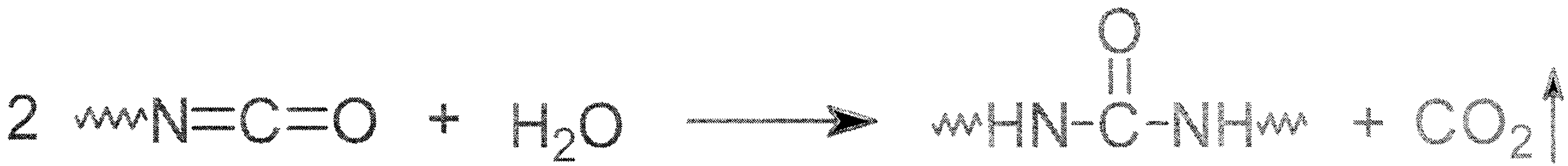
    evaporisation of liquid → dissipation of heat

- Reduction of thermal conductivity
- Viscosity cutter

    BA have low viscosity → easier processing

CHEMICAL BLOWING AGENTS

Water



Formic acid (AB method)

PHYSICAL BLOWING AGENTS

Chloro-fluoro-carbons	CFC
e.g. TCFM-11	$CFCl_3$
Hydro-chloro-fluoro-carbons	HCFC
e.g. HCFC-141b	CCl_2FCH_3
Hydrocarbons	HC
e.g. pentane isomers	$CH_3(CH_2)_3CH_3$
Methylene chloride	CH_2Cl_2
Liquid Carbondioxide	lq. CO_2

FLAME RETARDANTS

Main purpose: Inhibition of the burning process

By physical effects:

- Cooling of the substrate by endothermic decomposition
- Formation of solid or gaseous protective layers
- Dilution of inflammable materials

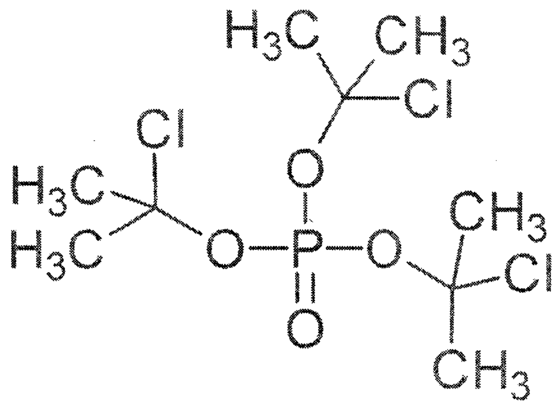
By chemical effects:

- Reaction in the gas phase. Interception of free radicals
- Reaction in the solid phase.
  Decomposition of the polymer

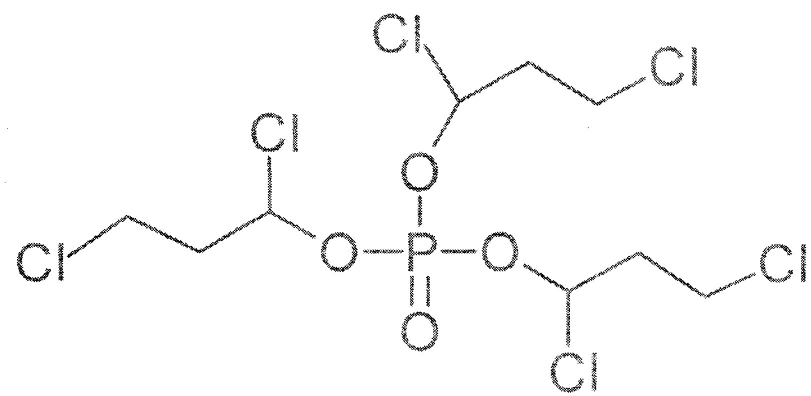
FLAME RETARDANTS

Liquid FRs

Halogen containing organic phosphates



TCPP



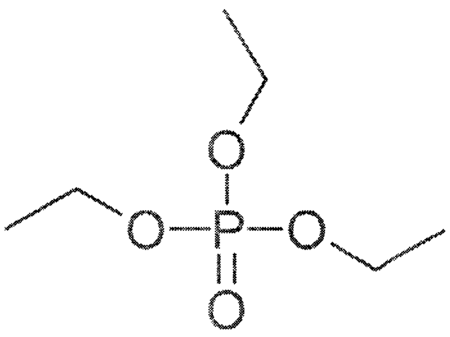
TDCP

FLAME RETARDANTS

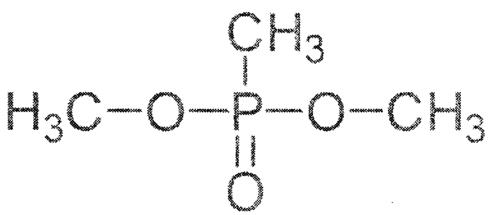
Liquid FRs

Halogen containing organic phosphates

Halogenfree organic phospates



TEP



DMMP

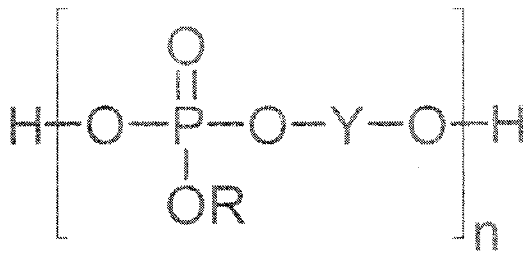
FLAME RETARDANTS

Liquid FRs

Halogen containing organic phosphates

Halogenfree organic phospates

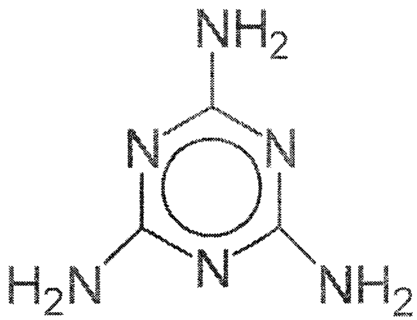
Halogenfree phosphorous polyols (be incorporated)



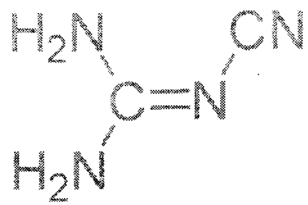
FLAME RETARDANTS

Solid FRs

Nitrogen enriched chemicals



Melamine



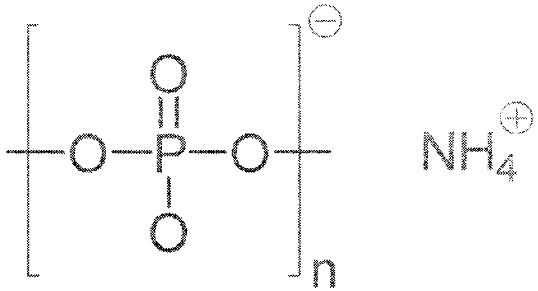
Dicyandiamide

FLAME RETARDANTS

Solid FRs

Nitrogen enriched chemicals

Polyphosphates



FLAME RETARDANTS

Solid FRs

Nitrogen enriched chemicals

Polyphosphates

Metal oxides and hydroxides

$$2\ Al(OH)_3 \xrightarrow{\text{heat}} Al_2O_3 + 3\ H_2O$$

STANDARD TEST METHODS

FOR

POLYURETHANES

INPUT Institute for Polyurethane Technology

International and National Standards

•	ISO	International Standard Organisation
•	ASTM	American Society for Testing and Materials
•	DIN	Deutsches Institut für Normung
•	BSI	British Standards Institution
•	NF	Francaise de Normalisation

Title of test method	PU type	ISO No.	ASTM No.	BS No.	DIN No.	NF No.
SI units and recommendations for their use	All	1000 (1973)	E 380-89 E 62-84	5555:1981 (1989)	-	-
Conditioning of test specimen	All	291 (1977) 554 (1976)	D 618-61 (1981)	2782: (1982)	50014 50005	-
Preferred test temperatures	All	3502 (1976)	D 618-61 (1981)	2782: (1982)	50014	-
Constant humidity cabinets using aqueous solutions	All	R483 (1976)	E 104-85	3718: 1964 (1984)	50014	-

Title of test method	PU foam	ISO No.	ASTM No.	BS No.	DIN No.	NF No.
Determination of linear dimensions of test specimen	Rigid	1923 (1981)	D 1622-88	4370:Part 1 1988	53420	-
Determination of the apparent density of cellular materials	Rigid	845 (1984)	D 1622-88	4370:Part 1 1988	53420	-
Compression test of rigid cellular materials	Rigid	844 (1985)	D 1621-73	4370:Part 1 1988	53421	T56-101
Bending test for rigid cellular materials	Rigid	1209 (1976)	D 790-86 D 790M-86	4370:Part 1 1988	53423	T56-102
Determination of tensile properties of rigid cellular materials	Rigid	1926 (1979)	C 203-85	4370:Part 2 1973	53430	T56-103

Title of test method	PU foam	ISO No.	ASTM No.	BS No.	DIN No.	NF No.
Determination of shear strength of rigid cellular materials	Rigid	1922 (1981) R/1663	C 273-61 (1988)	4370:Part 2 1973	53427	T56-118
Determination of apparent thermal conductivity by means of heat flowmeter	Rigid	2581 (1975)	C 518-85	874:Part 2 1988	52616	T56-124
Determination of apparent thermal conductivity by guarded hot-plate	Rigid	2582 (1980)	C 177-85	4370:Part 2 1973	52612	X10-21
Test for dimensional stability of rigid cellular materials	Rigid	2796 (1986)	D 2126-87	4370:Part 1 1988	53431	T56-122
Determination of temperature at which permanent deformation occurs under compressive load	Rigid	7616 (1986)	D 621-64 (1988)	-	53424	-

Title of test method	PU foam	ISO No.	ASTM No.	BS No.	DIN No.	NF No.
Determination of water absorption by immersion method	Rigid	2896 (1987)	D 2842-69 (1975)	-	53433	-
Determination of water vapour transmission of rigid cellular materials	Rigid	R/1663	E 96-80	4370:Part 2 1973	53429	T56-105
Determination of the closed-cell content of cellular materials	Rigid	4590 (1986)	D 2856-87	4370:Part 3 1988	--	
Determination of the friability of cellular rigid materials	Rigid	DP 6187 (1985)	C 421-88	4370:Part 3 1988	-	T56-109

Title of test method	PU foam	ISO No.	ASTM No.	BS No.	DIN No.	NF No.
Measurement of the dimensions of test specimen	Flexible	1923 (1981)	D 3574-86	4443:Part 1 1988	53570	T56-119
Determination of tensile strength and elongation at break	Flexible	1798 (1976)	D 3574-86 D 3543-80	4443:Part 1 1988	53571	T56-108
Determination of compression set	Flexible	1856 (1980)	D 3574-86	4443:Part 1 1988	53572	T56-112
Determination of hardness (indentation technique)	Flexible	2439 (1980)	D 3574-86	4443:Part 2 1988	53576	T56-111
Accelerated ageing test	Flexible	2440 (1972)	D 3574-86	4443:Part 4 1976	53578	T56-117

Title of test method	PU foam	ISO No.	ASTM No.	BS No.	DIN No.	NF No.
Determination of compression stress / strain characteristic and value	Flexible	3386/1 (1979)	D 3574-86	4443:Part 1 1988	53577	T56-110
Test for dynamic fatigue by constant load pounding	Flexible	3385 (1982)	D 3574-86	4443:Part 5 1980	53574	T56-114
Determination of tear strength of flexible foam	Flexible	-	D 3574-86	4443:Part 6 1980	53575	T56-109