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Spray Foam Chemistry:

How it has changed over the years

HOW DOES IT IMPACT FOAM PROCESSING AND QUALITY?

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Mary Bogdan is a Research Fellow for Honeywell and is the Technology Lead for the Blowing Agent Technical Sales and Service Group. She earned a bachelor's degree in Chemistry/Biochemistry and an MBA from Canisius University. Since joining Honeywell in 1989, Mary has held numerous positions in research and development. She currently supports the global fluorine products blowing agent business.

Over her career, she has worked on the introduction of Honeywell's HCFC, HFC and HFO technology across many applications. She is a Six Sigma Black belt. She has more than 30 U.S. patents and has numerous published technical articles on the development and use of fluorocarbons as foam blowing agents. She has co-authored and presented several CPI papers receiving the CPI Best paper awards for 12 of her presentations. She has received a Distinguished leadership award from ACC CPI and a Heroes in Chemistry Award from the ACS.

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Rick brings more than 25 years of experience in technical marketing, building science, and product/business development delivering new materials and applications to the construction market. Drawing from his prior teaching experience, Rick simplifies complex building envelope issues and clearly describes solutions for construction and design professionals. Rick served as technical director of SPFA from 2008-2020, and as executive director from 2020 to 2024. As a technical consultant to SPFA, he oversees all technical activities for the organization. He holds a Ph.D. in Engineering Science and Mechanics Penn State, MSME from Bucknell and a BSME from the University of Maryland. Rick is a Registered Professional Engineer in Pennsylvania.

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Agenda

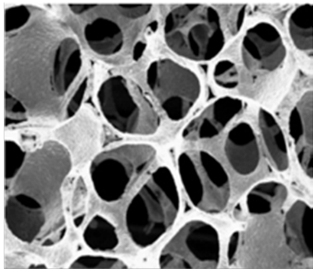
- What is foam plastic?
- SPF- The Reaction
- SPF- The History
- SPF- The Reaction Components
  - A-side-MDI
  - B-side
    - Polyols
    - Blowing Agents
    - Flame Retardants
    - Surfactants
    - Catalysts
  - SPF- Generic Systems Over Time
  - Conclusions- What's next?

SPF – What is foam plastic?

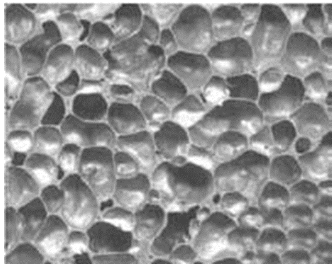
A mass of gas bubbles, or cells, in a matrix

In a plastic foam, a plastic (polymer) is the matrix

- Open cell foams
  - Gas in cells not critical
  - Properties of polymer matrix critical
- Closed cell foams
  - Typically 97+% (by volume) gas
  - Gas in cell contributes to properties of foam
  - The gas (the blowing agent)
    - expands the foam
    - contributes to foam properties, especially for thermal insulation foams



Open Cell Foam



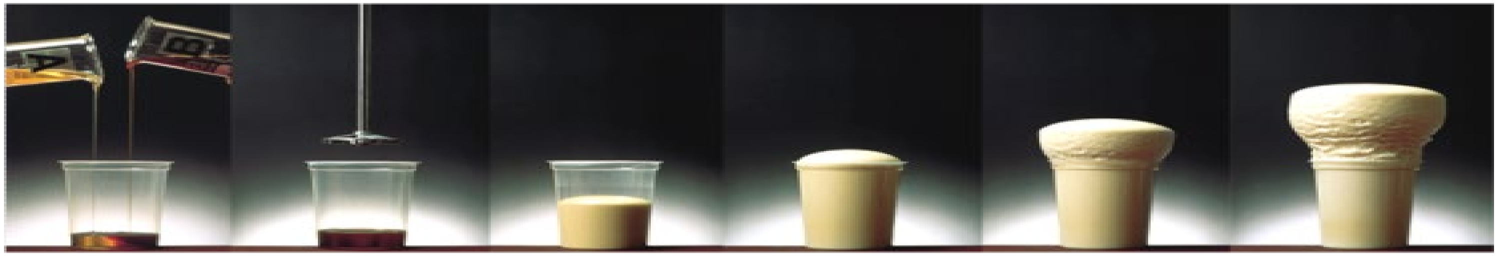
Closed Cell Foam

SPF – The Reaction

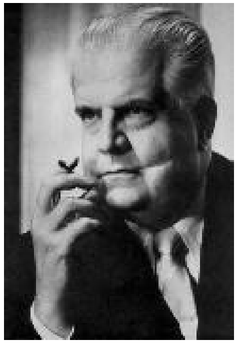
Reaction of two basic chemical ingredients

R - (N=C=O)X **ISOCYANATE**	**+**	**R' - (OH)Y** **POLYOL**	**Exothermic** →	**O** **||** **R - N-C-O-R'**
Isocyanate		**Resin Blend**		**POLYURETHANE** **FOAM**

Charred Foam



SPF- The History



- **Late 1800's -** first process for MDI invented
- **1937** - German scientist Otto Bayer received patent for polyurethane chemical reaction
- **1940-1950:** MDI used in military applications
- **1950- 1960:** 1953- Blendometer invented (first foam machine) – Walter Baughman, Polyether polyols introduced, First commercial foam use- seal rail car roofs
- **1960- 1970:** 1963- Fred Gusmer invented spray machine and gun (low pressure to high pressure), SPF adoption increasing, First spray foam roof, Fires result in increase flame retardant requirements, Hydraulic proportioners offered
- **1980- 1990:** -Lead catalysts no longer used, Tin catalysis, HCFC-141b, Energy Crisis- increased insulation use
- **1990-2010:**- HFC technology, Increasing energy code requirements
- **2010- Today:** Biobased polyols begin to appear, HFO technology, Reactive flame retardants and catalysts, PCP program, Sustainability/ Green Technology

SPRAY POLYURETHANE FOAM ALLIANCE

The Reaction Components

Reaction of two basic chemical ingredients: 1:1 Reaction by volume

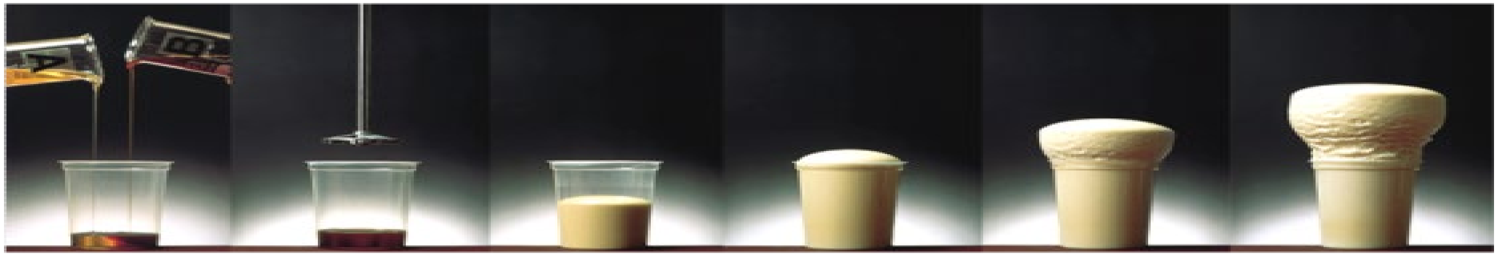
Isocyanate "A"
Basic Component

+

Resin "B"
Consists of at least 5 components:
- **Polyols**
- **Surfactants**
- **Catalyst**
- **Blowing Agents**
- **Fire Retardants**

+

HEAT
Exothermic reaction



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A-side
Methylene diphenyl diisocyanate (MDI)

A-side
Methylene diphenyl diisocyanate (MDI)

Commonly referred to as MDI, Iso, isocyanate, MDI, PMDI & just A-Side.

The A-Side is typically a mixture of:

~ 50% methylene diphenyl diisocyanate (MDI)

~ 50% polymeric methylene diphenyl diisocyanate (pMDI)

98%4,4’, 2% 2,4’ ~ 50% functional

A-side
Methylene diphenyl diisocyanate (MDI)

Generic Manufacturing Process

Nitration (Benzene+ Nitric acid + Catalyst)

Hydrogenation (Nitrobenzene + Hydrogen + Catalyst)

Aniline/Formaldehyde Condensation (Aniline + Formaldehyde + Catalyst)

Phosgenation (MDA/DADPM + Phosgene)

Separation, Differentiation, Purification (Distillation/ Fractionation)

Note: Manufacturing may vary by individual manufacturing process

Variations in viscosity and reactivity differentiate products

Not all MDI the same- Matched by System house to B-side

B-side
Polyol Resin System – Closed Cell Foam

Resin is a blend of several chemical compounds.

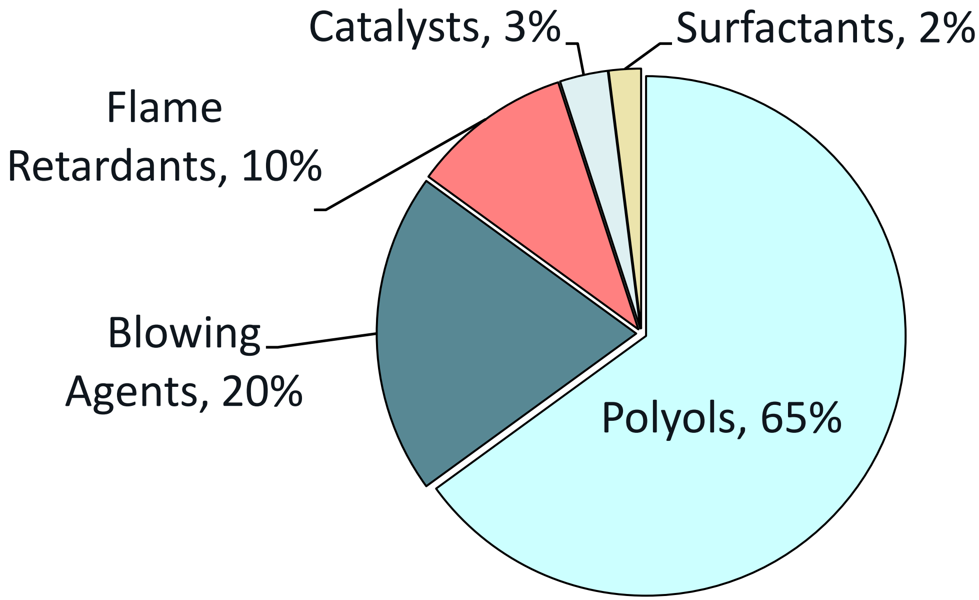
Classification of these compounds are shown below

Actual proprietary blends may use multiple chemicals within each class

1. **Polyols**
2. **Blowing Agents**
3. **Flame Retardants**
4. **Surfactants**
5. **Catalysts**

→ **Proprietary blend of additives affect cell formation & foam performance**

General Resin (Polyol) Blend "B"



Comparison of Resin (Polyol) Blend “B”

Typical Composition of a Polyol Resin in SPF Systems

Component	Low Density Open Cell	Medium Density Closed Cell
Polyol	35-60%	40-65%
Blowing Agent	18-24%	7-15%
Catalyst	3-8%	3-10%
Flame Retardant	15-25%	15-25%
Surfactant and Glycerin	0.5-8%	1-8%

Resin (Polyol) Blend "B" - Polyols

Polyols

- React with Isocyanate
- Made from variety of materials
- Foam physical properties and application environment dictate what polyols are used.
- Often a blend contains more than 1 type of polyol
- Two Main Classifications:
  - Polyether
  - Polyester

Resin (Polyol) Blend "B" - Polyols

Common Generic Reaction :
Propylene oxide + Initiator + Catalyst (acid, base, metal) ➡Neutralize , Dry
Wide variety of types of final polyols

- R = sucrose, sorbitol, glycerine, toluenediamine, water, ethylene glycol, triethanolamine, 4,4'-diaminodiphenylmethane, phenol/formaldehyde condensation resin, others and mixtures
  - Defines functionality and reactivity
  - Major influence on foam properties
  - Defines miscibility with blowing agents

- Alkylene Oxide (ethylene, propylene, butylene)
  - Defines reactivity (ethylene > propylene > butylene)
  - Defines molecular weight
  - Defined miscibility with blowing agents

SPFA SPRAY POLYURETHANE FOAM ALLIANCE

Resin (Polyol) Blend "B" – Polyester Polyols

Added to a foam to lower cost and improve fire resistance

Three major types

- Transesterified bottoms from dimethylterephthalate (DMT) process
- Glycolysis of recycled PET (bottles, film)
- Esters of phthalic anhydride

Differentiation

Ester type
Molecular weight (number of glycol units)
Functionality (glycerine co-fed with glycols)
Additives
Viscosity diluents
Compatibilizers
Flame retardants

Resin (Polyol) Blend "B" - Blowing Agents

97% volume of the foam is blowing agent (cell gas)

B-side polyol resin blend typically contains less than 20% by weight of blowing agents

Two types of blowing agents

Chemical- reacts with MDI- generates gas + heat (Water)

Physical- heat from reaction causes blowing agent to vaporize + expands the foam

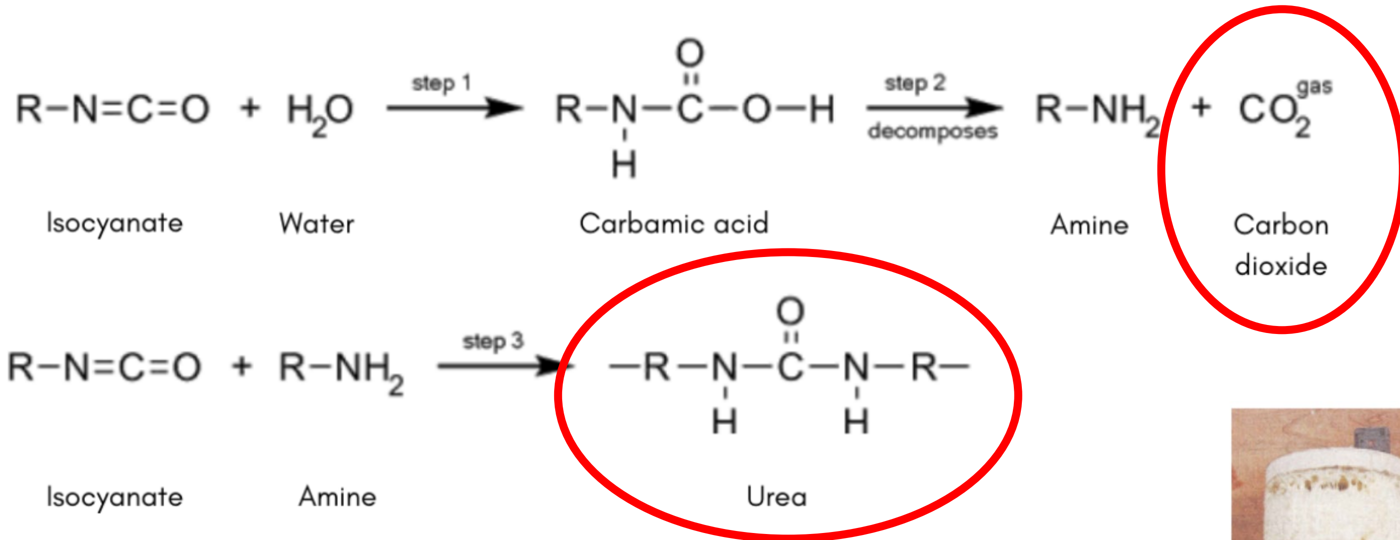
Enovate 245fa: 1,1,1,3,3-pentafluoropropane, HFC-245fa, $CF_3CH_2CF_2H$- Stop Production 1/2025

Solstice LBA: Trans- 1-chloro-3,3,3- trifluoropropene, HFO-1233zd(E), (E)$CF_3CH{=}CHCl$

Solstice GBA: (E) trans-1,3,3,3- tetrafluoropropene, HFO-1234ze(E), (E)$CF_3CH{=}CHF$

Opteon 1100: Cis-1,1,1,4,4,4-Hexafluoro-2-butene, HFO-1336mzz-Z, $CF_3CHCHCF_3$

Resin (Polyol) Blend "B" - Blowing Agents - Chemical



Not Ideal Polymer

Friable, Poor Adhesion

Wet Surface

Resin (Polyol) Blend "B" - Blowing Agents - Physical

Molecular weight- moles of gas- critical

Boiling point of the blowing agent

- Blowing agent must be in the gas phase to be effective

Vapor phase thermal conductivity of the gas

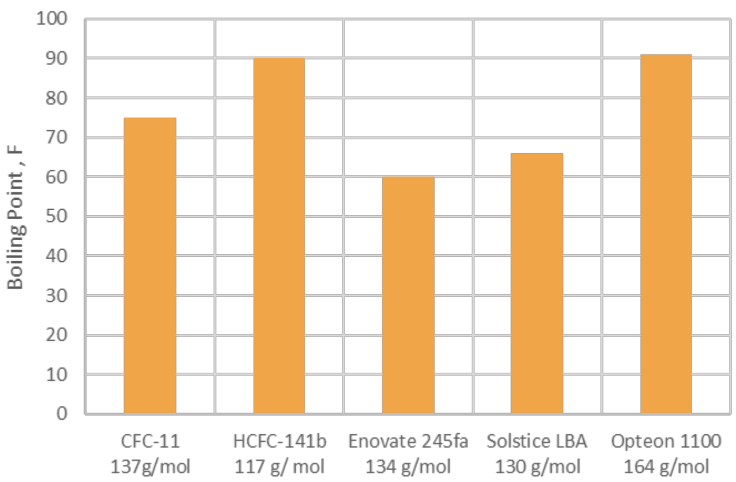
- Fluorocarbons are among the best

Presence of other gases in the cell

- Air, nitrogen, or CO_2 can negatively influence thermal conductivity

Solubility of the blowing agent in the polymer

Diffusion rate of the blowing agent out of the foam, CO_2 out and air into foam



Physical- heat from reaction causes blowing agent to vaporize + expands the foam

SPRAY POLYURETHANE FOAM ALLIANCE

Resin (Polyol) Blend "B" - Flame Retardants

Flame Retardants are typically 15- 40 % of polyol resin system.

- Used to reduce foam combustibility - Necessary for code requirements
- Two types - Reactive and Unreactive

Resin (Polyol) Blend "B" - Flame Retardants - Unreactive

Unreactive: Positive impact on adhesion, shear, and tensile strength

- Tris (2-chloroethyl(or propyl) phosphate (TCPP)
- Dimethylmethylphosphonate (DMMP)
- Triethylphosphate (TEP)

Generic TCPP Process : ***Phosphorous oxytrichloride with propylene oxide in the presence of a catalyst***.

Resin (Polyol) Blend "B" - Flame Retardants - Reactive

Reactive (Contains -OH groups that react with isocyanates) incorporated into polymer

- Tetrabromophthalic anhydride esters
- Di (and Tri) bromoneopentyl glycol
- Mixtures

Resin (Polyol) Blend "B" - Flame Retardants

Differentiation between FR

- Halogen used to prevent surface burning
  - Free radical mechanism
- Char formation: Phosphorous , Aromatic structures
- Chemical composition impacts solubility, FR performance, foam properties
  - Aliphatic vs aromatic halogen impacts stability
  - Non-reactive flame retardants can plasticize the foam
    - Negative impact on dimensional stability and compressive strength
    - Positive impact on adhesion, shear, and tensile strength

Resin (Polyol) Blend "B" - Surfactants

Surfactants are typically 1-2% of polyol resin system.

- Include silicone polymers which typically have low toxicity by all routes of entry into the body.

Silicone based fluids used for several purposes in foam

- Emulsify polyol and isocyanate to ensure homogeneous foam
- Solubilize polyol blends to create stable premixes
- Control cell size through surface tension modification
- Control amount of open and/or closed cells

Multiple types available

Resin (Polyol) Blend "B" - Surfactants

Differentiation

- Chemical structures define performance
  - SiC content in backbone
  - SiOC content in backbone
  - Polyether pendant groups:
    - Type (Ethylene vs propylene oxide)
    - Number per molecule
    - Size (molecular weight)
    - End capping (reactive vs non-reactive)

Resin (Polyol) Blend "B" - Catalysts

Catalysts promote reaction between polyol and A-side.

Amines typically contains 1 to 5% amine catalyst and metals <1%

Two Main Classes: Amines (Traditionally tertiary) and Metals

Amines: Non-reactive and Reactive

- Catalyzes isocyanate - polyol and isocyanate - water reaction
- Dozens of varieties designed for specific reactivity, stability, and cure rate
- Associated with foam odor (fish smell)

Metals:

- Reactivity accelerator for very fast systems (e.g. spray)
- Curing catalysts

Resin (Polyol) Blend “B” - Catalysts

Metal or Ammonium Carboxylates

- Catalyzes isocyanurate reaction
- Reactivity accelerator for very fast systems (e.g. spray)
- Curing catalysts

Typical Examples= new technology emerging

- Potassium octoate, Potassium acetate
  - Isocyanurate (trimer) reaction
- Dibutyl tin dilaurate
  - Strong catalyst for isocyanate - polyol reaction
  - For fast reacting systems
- Quarternary ammonuim carboxylates for trimerization reaction
- Bismuth
- Zinc

Resin (Polyol) Blend "B" - Generic System Over Time

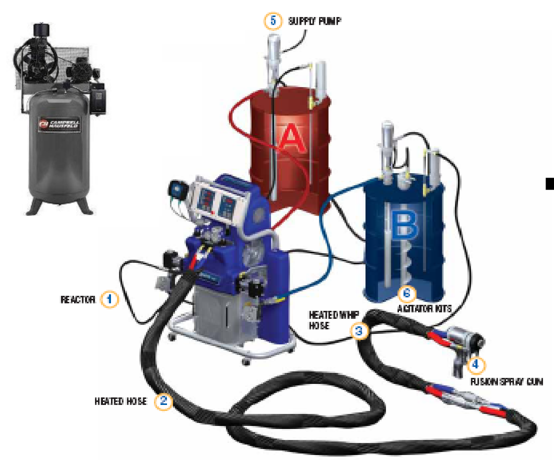
Changes over time to meet changes in raw materials and product requirements

Each change may impact field processing

Formulation	CFC	HCFC	HFC	HFO
Polyester Polyol	35	50	60	60
Polyether Polyol	65*	50*	40*	40*
Additive	3	2	0-2	0-2
Surfactant	1	1-2	1-2	1-2
Catalyst- Amine	1	1-3	1-3	1-3
Catalyst - Metal	0.1-0.5	0.5	0.5	0.5-1.5
Flame Retardant	7	7	10-15	10-15
Water	0.5-1	0.5-1	2-3	2-5
Fluorocarbon Blowing Agent				
CFC-11	30			
HCFC-141b		25		
HFC-245fa			8-12	
HFO- Technology				8-12

HFC- HFO Changes

Foam Manufacturing Process



- A side and B side are pumped through a heated proportioning pump
- Pass thru heated hoses separately
- “A” & “B” mix at gun and react

- Applied to substrate
- Generates heat
- Blowing agent vaporizes- forms bubbles
- Solid foam plastic

Consider the Differences

The table below compares the physical properties of the SPF*.

Characteristic*			
Type	Open	Closed	Closed
Use	Building envelope internal	Building envelope Internal & external	Roof Insulation
Density	0.5-1.1	1.8-2.5	2.5-3.1
R-value/in	3.8	6.5	6.4
Closed cell content, %	<10	>93	>90
Compressive strength, psi	3	16 – 43 (AVE 26)	40-60 (AVE 49)
Tensile Strength, psi	3 - 37 (AVE 7)	22-202 (AVE 57)	55 - 90 (AVE 71)
Air infiltration	0.02	0.02	-
Vapor perm (perms)	35.5 (11-97)	2 - 3.0	2.1
Water absorption g/cc	56	0.42	0.24
Water absorption % Vol	41	<1	<1

Application Considerations

Liquid Components Properties*		
Property	Isocyanate A-PMDI	SEALECTION® 500 Resin
Color	Brown	Amber
Viscosity @ 77°F (25°C)	180 – 220 cps	150 – 300 cps
Specific Gravity	1.24	1.08 – 1.12
Shelf Life of unopened drum properly stored	12 months	12 months
Storage Temperature	50 – 100°F (10 – 38°C)	50 – 100°F (10 – 38°C)
Mixing Ratio (volume)	1:1	1:1

*See MSDS for more information.

Reactivity Profile			
Cream time	Gel time	Tack free time	End of rise
1 – 2 seconds	3 – 4 seconds	6 – 7 seconds	6 – 7 seconds

Recommended Processing Conditions*		
Initial Primary Heater Setpoint Temperature	130°F	54°C
Initial Hose Heat Setpoint Temperature	130°F	54°C
Initial Processing Setpoint Pressure	1200 psi	8274 kPa
Substrate & Ambient Temperature	> 23°F	> -5°C
Moisture Content of Substrate	≤ 19 %	≤ 19 %
Moisture Content of Concrete	Concrete must be cured, dry and free of dust and form release agents.	

Conclusions

Relatively short history for technology

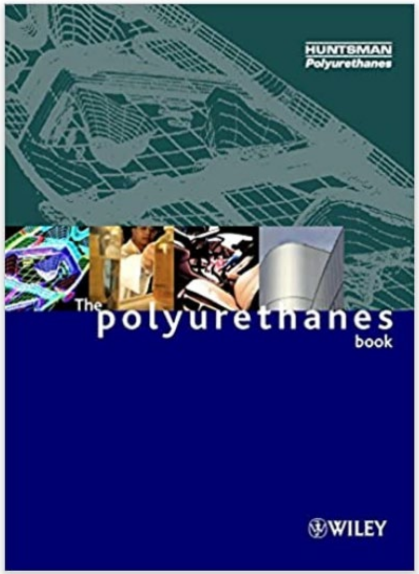
Industry has made substantial transitions and improvements to:

- Equipment
- Raw materials
- Training

Ideal, sustainable solution to insulate building

Continued success is a team effort: Contractors, System houses, Raw material suppliers

References and Acknowledgements



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It is a team effort that develops new technology. Get involved.