

CYTEC

CHEMISTRY AND PROPERTIES OF BLOCKED ALIPHATIC ISOCYANATES

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3,5-Dimethylpyrazole (DMP) Blocking of Cytec's Aliphatic Isocyanates

1. Overview:

Cytec's aliphatic isocyanates are DMP blocked in approximately 50% refluxing heptane. The rate of heat evolution and therefore the maximum reaction temperature may be controlled by the slow addition of the isocyanate. The maximum allowable reaction temperature is 100°C. The reaction rate is determined by analyzing for % unreacted NCO using IR and/or titration. At the end of the reaction, the reaction mixture is allowed to cool to room temperature. Our TMI® (Meta) aliphatic isocyanate is a liquid when DMP blocked and is stripped free of heptane under vacuum. At this time, it is unknown what physical form our other DMP blocked products may take. Crystalline products should be vacuum filtered from the heptane and washed once with fresh cold heptane. They may be oven dried in a forced air oven at 49-50°C and packaged without further purification.

2. Procedure:

Charge 578.7 grams of DMP (6.02 moles) to a 5 liter, 3 neck, round bottom flask equipped with a reflux condenser, stirrer and thermocouple. Charge 1881.6 grams of heptanes to the reactor. Blanket the reactor with nitrogen and heat to reflux. An oil bath heated to 90-100°C is used as the heat source for the reactor. The DMP will not dissolve at room temperature, but the white slurry will turn to a bluish haze as the reactor is heated and the material dissolves. The DMP should be completely dissolved when the reaction temperature reaches 75°C. Once the material is all dissolved, the addition of the isocyanate can begin. The bath temperature at this point is 96°C and the reactor temperature is 70°C. Using an addition funnel, add Cytec's aliphatic isocyanate (equivalent to 5.96 moles of NCO) to the reactor in a total time of forty-one minutes. The maximum reactor temperature is 88°C. Hold the reaction at reflux conditions for a total time of eighty-eight minutes. A sample taken at this point will show no isocyanate present via FTIR. Remove the oil bath and allow the batch to air cool down to room temperature overnight (17 hours) with slow stirring. Liquid samples are roto-evaporated to remove Heptane at a maximum of 70°C and 7 mm Hg absolute pressure. Crystalline samples are vacuum filtered to separate the product from the heptane. The crystalline material is washed with two liters of -15°C heptane. Crystalline product may be dried in a forced air oven at 49-50°C to a constant weight (generally overnight). The material collected had a molar yield of 85 percent.

3. Product Analysis:

The free NCO should be <0.05 Wt% via dibutylamine titration. A 15-gram titrated sample reveals no detectable NCO. The free DMP should be no more than 1.0 Wt% via Isothermal GC at 65°C.

2-Butanone Oxime (MEKO) Blocking of Cytec's Aliphatic Isocyanates

1. Overview:

Cytec's aliphatic isocyanates are MEKO blocked at 45-52°C. this oxime blocking is an exothermic reaction and the heat of reaction is removed by cooling water. The rate of heat evolution and therefore the maximum reaction temperature may be controlled by the slow addition of MEKO. The maximum allowable reaction temperature is 52°C. The reaction rate is determined by analyzing for % unreacted NCO using IR and/or titration. At the end of the reaction, the reaction mixture is cooled to room temperature. The product is packaged without further purification.

2. Procedure:

Charge the Cytec isocyanate (equivalent to 2.02 moles of NCO) to an appropriate sized round bottom flask purged with nitrogen. Blanket the reactor with nitrogen. Stir the isocyanate at 60-80 rpms. Add 177.7 grams of MEKO (2.04 moles) over 60 minutes, via two additions of ~89 grams. One-half the MEKO may be added in 15 minutes and the remainder added over 45 minute. Typically, the temperature rises equals 42-47°C. Stir for an additional one-half hour maintaining a temperature of 42-45°C. The batch is water cooled to room temperature and checked by IR for disappearance of the NCO band.

3. Product Analysis:

The free NCO should be <0.05 Wt% via dibutylamine titration. A 15-gram titrated sample reveals no detectable NCO. The free MEKO should be no more than 1.0 Wt% via Isothermal GC at 65°C.

Caprolactam Blocking of Cytec's Aliphatic Isocyanates

1. Overview:

e-Caprolactam is reacted with Cytec's isocyanates in approximately 50 weight percent refluxing heptane. It is a slightly exothermic reaction and the heat of reaction is controlled by the refluxing heptane. The rate of heat evolution and therefore the maximum reaction temperature may be controlled by the slow addition of the isocyanate. The maximum allowable reaction temperature is 100°C. The reaction rate is determined by analyzing for % unreacted NCO using IR and/or titration. At the end of the reaction, the reaction mixture is allowed to cool to room temperature. Our isocyanate products will crystallize as a white slurry in heptane. These products are vacuum filtered from the heptane and washed once with fresh cold heptane. They are oven dried in a forced air oven at 49-50°C. and packaged without further purification.

2. Procedure:

Charge 681.6 grams of e-Caprolactam (6.02 moles) to a 5 liter, 3 neck, round bottom flask equipped with a reflux condenser, stirrer and thermocouple. Charge 1881.6 grams of heptanes to the reactor. Blanket the reactor with nitrogen and heat to reflux. An oil bath heated to 90-100°C is used as the heat source for the reactor. The e-Caprolactam will not dissolve at room temperature, but the white slurry will turn to a bluish haze as the reactor is heated and the material dissolves. The e-Caprolactam should be completely dissolved when the reaction temperature reaches 75°C. Once the material is all dissolved, the addition of the isocyanate can begin. The bath temperature at this point is 90°C and the reactor temperature is 80°C. Using an addition funnel, add Cytec's aliphatic isocyanate (equivalent to 5.96 moles of NCO) to the reactor in a total time of fifty minutes. The maximum reactor temperature is 99°C. Hold the reaction at reflux conditions for a total time of four hours and thirty minutes. A sample taken at this point will still show some isocyanate present via FTIR. The value of the isocyanate (2256cm⁻¹)/ C-H stretching (2972cm⁻¹) should be about 0.66. The conversion of isocyanate at this time is calculated to be approximately 80 percent. Remove the oil bath was and allow the clear batch to air cool down to room temperature overnight (17 hours) with slow stirring. In the morning the reactor will contain a white slurry. Vacuum filtration is performed to filter the product from the heptane. Wash the product with two liters of -15°C. heptane. Dry the product using a forced air oven at 49-50°C to constant weight (generally overnight). The material collected equaled a molar yield of 86-87 percent.

3. Product Analysis:

The free NCO should be <0.01 Wt% via dibutylamine titration. A 30-gram titrated sample reveals no detectable NCO. A KBr pellet made from the material shows no isocyanate absorbance at 2257 cm⁻¹ by Infrared Spectroscopy. A melting point of the product is performed using a capillary melting point device heating at 1°C per minute. e-Cap blocked TMI[®] (META) Unsaturated

Aliphatic Isocyanate melting point is 70°C and e-Cap blocked TMXDI® (META) Aliphatic Isocyanate melting point is 117°C. The residual e-Caprolactam analyzed by gas chromatography should be less than 1 percent at a 70°C injection temperature using a 2.10 gram sample of the product in 100 cc. of methylene chloride.

Alcohol Blocking of Cytec's Aliphatic Isocyanates

1. Overview:

Alcohol is reacted with Cytec's isocyanates in approximately a 5-15/1 molar ratio of alcohol to isocyanate. Lower amounts of alcohol can be used if catalysts are used to facilitate the reaction. Higher amounts of alcohol are required for less reactive alcohols. We try to stay away from using catalyst because most catalyst will stay with the product. Reactions may be slightly exothermic and the heat of reaction can be controlled by the refluxing alcohol. The rate of heat evolution and therefore the maximum reaction temperature may be controlled by the slow addition of the isocyanate. The reaction rate is determined by analyzing for % unreacted NCO using IR and/or titration. At the end of the reaction, the reaction mixture is stripped of the alcohol. Our isocyanate alcohol blocked products will slowly crystallize as the reaction mixture is cooled. Of course, this depends on the melting point of the product. The products are packaged without further purification.

2. Procedure:

Charge to a 3 neck, round bottom flask purged with nitrogen, the alcohol. If catalyst is used it should be added here. Blanket the reactor with nitrogen and heat to reflux. Add Cytec's isocyanate containing products slowly, monitoring any rise in exotherm. Batch conversions are monitored by IR for disappearance of the NCO band. After ~3 hours at reflux, most reactions were essentially complete.

3. Product Separation and Purification.

Successful separation was performed by stripping the reaction mixture in a roto-evaporation unit under vacuum. The molten products are poured to half fill a plastic container. Products with low melting points (~30-60 °C) crystallized after two days at room temperature, see below for removal instructions.

Removal Of Cytec's Alcohol Blocked Aliphatic Isocyanates From Plastic Containers

1. Due to the nature of these materials, proper personal protection equipment should be used during this procedure.
2. The alcohol blocked materials are brittle solids, especially at low temperatures. If possible, place the container in a refrigerator overnight. Pound the outside of the plastic container with a rubberized hammer to break up the solid block.
3. Transfer the chunks and powder to dry containers. If the chunks are too large to handle they can be ground in a grinder.

Further Crystallization

The products with high melting points may be further crystallized by taking 25 grams of the stripped solution and dissolving in 50 grams of methanol. Try cooling to crystallize at this point. If unsuccessful, an additional 50 grams of DI water may be added and the mixture cooled to 5°C with an ice bath. Crystals formed can be filtered and dried in an oven at 60°C. Essentially a 100% yield of a waxy like material is obtained in most cases.



**Isocyanate Onset Temperatures of Blocked Isocyanates Based on Cytec's
TMXDI® (Meta) Aliphatic Isocyanates**

Blocking Group	NCO Onset by FTIR Deblock Temperature, °C
3,5-Dimethylpyrazole	55-65
2,6-Dimethyl-4-Heptanone Oxime	60-75
Methyl Ethyl Ketoxime	65-80
2-Heptanone Oxime	70-80
1,2,4-Triazole	80-90
ε-Caprolactam	95-105
Nonylphenol	145-165
t-Butanol	150-185
Propylene Glycol	>180
Isopropanol	190-210
Methanol	200-220
n-Butanol	200-230
n-Hexanol	215-230
n-Pentanol	215-235

Cure Temperatures of Blocked TMI Self-Crosslinking Copolymers

<u>Blocking Agent</u>	<u>Temperature¹, °C</u>
Methyl ethyl ketoxime	120
N-Hydroxysuccimide	130
ϵ -Caprolactam	135

¹ Films cured for 30 minutes. Temperature required to achieve 200 MEK double rubs without marring coating.



**Physical Attributes of Blocked Isocyanates Based on
Cytec's Aliphatic Isocyanates**

Cytec Isocyanate	Blocking Material	Physical State	Melting Point °C
m-TMI	MEKO	Liquid	-
	3,5-Dimethylpyrazole	Liquid	-
	n-butanol	Solid	~27
	Methanol	Solid	~37
	t-butanol	Solid	~60
	ε-Caprolactam	Solid	~70
	Nonylphenol	Solid	~80
m-TMXDI	MEKO	Resinous	-
	n-Butanol	Solid	~68
	ε-Caprolactam	Solid	~117
	1,2,4-Triazole	Solid	~117
	Acetone Oxime	Solid	~125
	Methanol	Solid	~130
Cythane	MEKO	Solid in BuOAc	Oligomer