MDI-based Flexible Foam in Pillow Manufacture

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ABSTRACT

There has been resistance to using MDI for flexible urethane foams because of a long-held perception that this molecule 1) does not react as rapidly, nor 2) give foams of the same quality. It is the purpose of this paper to show that MDI based flexible foams, blown with ecomate© blowing agent, can produce foams with superior soft touch and ease of processibility.

When used in molded pillow manufacture, the foams are easier to process, use less isocyanate, and require less heat in molds, and give earlier demold times. In addition, they have superior whiteness, and less residual odor than those foamed conventionally with TDI.

ISOCYANATE COMPARISON

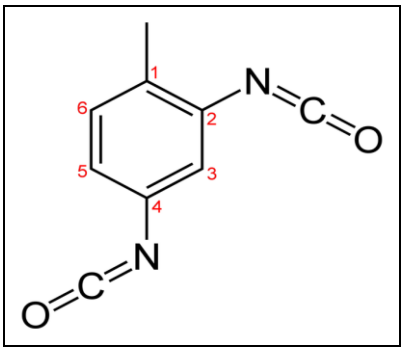

Figure 1: Toluene Di-isocyanate

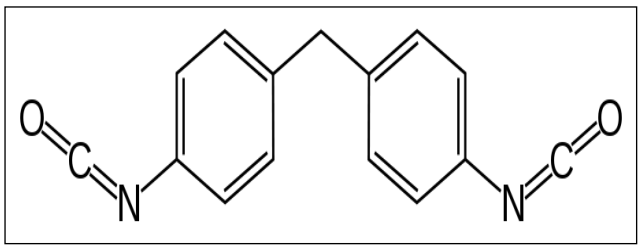

Figure 2: Pure 4,4'-Methylene Diphenyl Di-isocyanate

Flexible urethane formulators are very familiar with the chemical structures of MDI and TDI. They are quite aware of the difficulties in handling pure MDI [It is a solid at room temperature, melting at 40 C]. And like TDI, it comes in various isomers that have differing reactivity. The 4,4' isomer is the most reactive [the 4-position is approximately 4 times as reactive as the 2-position isomer]. To overcome the freezing proclivity of the material, an impurity may be added such as a small amount of carbodiimide, or a small amount of prepolymer may be formed. Both of these techniques tend to lessen the reaction speed of the monomer.

The methylene bridge of the MDI molecule can give this monomer potentially more flexibility as compared to the tight linkages formed by TDI. While this linkage is considered part of the "hard

segment" of polyurethane foam, and is masked by the use of very long chain diols or triols, using the same polyol and water mix with MDI should give potentially softer foam because of this greater flexibility in the hard segment. That is the purpose of this paper, to show that this is indeed possible. Especially if one uses the right physical blowing agent.

CHALLENGES

One of the challenges [seemingly perpetual] of TDI use is its cost. According to ICIS Pricing, the price of toluene has almost doubled since the beginning of the year, and is expected to move still higher based on snug supply. This puts the price of TDI currently nearly 25% higher than pure MDI [Fig. 3], and narrows the cost per equivalent. Of course, limited use of PMDI can help to lower cost/pound as well, although its use will increase functionality in the foam and be limited to ~10+% of the isocyanate.

The cost per pound of foam shown in Table 1 was calculated using a 1.0 Index for TDI foams and a 0.7 Index for MDI foams. It does not reflect the cost of catalysts and surfactants, but was assumed that those amounts would be the same for foams of the same variety of end use.

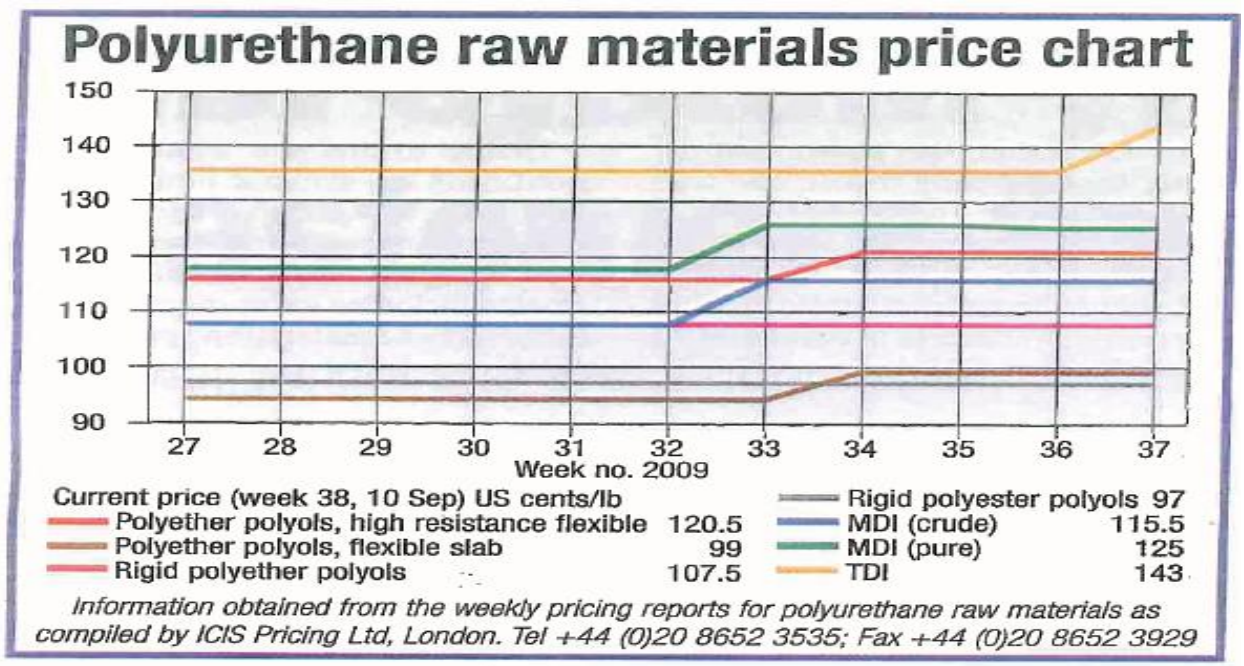

Figure 3: Current Pricing by ICIS Pricing LTD [Urethanes Technology International, Sept/Oct '09]

Table 1: Relative cost per pound of TDI v MDI foams

	EqWt	$/lb	~Cost*/lb Foam
TDI	87	1.43	1.025
MDI	125	1.25	1.039
PMDI	133	1.155	1.009

- Based on ICIS data above

Another challenge is supply. Recently [Oct 9th], Dow Chemical has declared *force majeure* (FM) on TDI at the company's Freeport Texas facility. "Complications resulting from a breakage of equipment have caused Dow to be unable to safely and properly produce TDI at Freeport, Texas, and we will be unable to ship or deliver full order quantities of TDI to our contract customers. Continued challenges with production are likely to persist for an extended period of time," the company said. "We will begin to allocate available TDI in a manner that is fair and reasonable and in accordance with contract terms." Dow did not have a time frame for the FM.

The number of Domestic TDI suppliers is dwindling which causes a less diversified supply chain. Dow is a major US TDI producer with more than 105,000 tonnes/year of capacity. Other major US TDI producers include BASF and Bayer.

MDI ADVANTAGES

One of the advantages of MDI is its low volatility. This is especially important in producing parts such as pillows which are lain upon for approximately 7.5 – 8 hours per day. Articles [such as pillows] made with MDI require a lower Foam Index for softness, which then helps insure all isocyanate is completely reacted. This required ratio and low volatility tends to favor MDI based foams for pillows.

BLOWING AGENTS

Now a few words about foam blowing agent choices. When R-11 was used for foam manufacture, the foams produced had a very soft touch [hand]. R-11 [CFC-11] was eliminated from use in foams around the world because of its ozone depletion potential [Montreal Protocol].

All Water blowing was attempted for super soft, low density foams, but the high exotherm of the water /isocyanate reaction results in a boardy foam with a strong potential of discoloration [scorch] and ultimately spontaneous combustion.

The conversion away from R11 led to the use of **methylene chloride** [dichloromethane], chosen because it's excellent solubility and non-flammability [Table 2]. Methylene chloride does not give the same 'hand' as R-11. It produces foams that are not as soft. In addition, despite being a chlorinated material, with no flash point, it does exhibit upper and lower flammability limits of 13% to 23% respectively. Environmentally, it has an atmospheric lifetime of 139 days and a GWP of 8.7. Most damaging for it, is that it is a suspect carcinogen [notably to the lung, liver, salivary and mammary glands] with a TWA of 25 ppm [86 mg/m3]. While not entirely banned, users must register its use and are limited to a small usage level of ~10,000 pounds per year.

Some formulators went to **Acetone** to blow their low density foams despite its high flammability [Flash point =-20C, LFL 2.5%, UFL 12.8%]. There currently exist some health concerns with the use of acetone as a blowing agent.

Other manufacturers bit the economic bullet and went the then most environmentally friendly route- **liquid CO2 blowing**. This allowed them to make the super soft, low density foams with good properties, but viscosity tended to be a challenge.

When the EPA declared acetone to be exempt VOC, many of these manufacturers petitioned the EPA decision [www.epa.gov/fedrgstr/EPA-AIR/1995/june/day-16/pr-752.html] stating they "may not be able to compete effectively if acetone is allowed unrestricted use as a foam blowing agent. They … face loss of their research investments and future profits if acetone is no longer regarded as a VOC, and therefore, no longer restricted In use." The EPA rejected the argument and exempted acetone in 1995.

Table 2: Blowing Agents for Flexible Foams

BA	CFC-11	MeCL2	ACETONE	ECOMATE
MW	137.4	84.9	58.1	60.5
BP, C	23.7	40.2	56.2	31.8
ODP	1	0	0	0
GWP	4600	8.7	1	1
VOC	EXEMPT	EXEMPT	EXEMPT	EXEMPT
MIR			0.56	0.06
FLASH PT	NONE	NONE	-20C	-19C
LFL	NONE	13%	2.6%	5.0%

A new entry into the blowing agent area is **ecomate®,** which has the most benign credentials of any foam blowing agent on the market today. While acetone appears to have very good environmental properties, it has a MIR value [indicative of smog production] over 9 times higher than ecomate. So, while it is exempted as a VOC by the EPA, its use will contribute to higher levels of smog than ecomate.

Some customers report that both methylene chloride and acetone tend to produce more scorching in foams than ecomate.

In addition, acetone is more flammable than ecomate: Having nearly the same flash point, ecomate has double the concentration by volume in air before becoming a flammable mixture. The heat of

combustion for acetone is nearly twice as high as that of ecomate [-28.5 KJ/g and -16.2 KJ/g respectively], indicating that almost twice as much energy is given off when acetone burns.

Apart from having wonderful environmental features, a foam blowing agent must also be able to produce all types of foam, at the various densities sold today to be a viable blowing agent candidate. Ecomate can do just that. In the US, it is being commercialized as the blowing agent in two companies' continuous slabstock lines. In South America, where 90% of the foam made is made in box pours, it has become a major contribution to certain customers' formulations.

Rather than talk about specifics of formulations, allow me to tell you of its impact in one company's molded pillow production. This company wanted to distance itself from highly volatile isocyanates, so they developed MDI-based formulations. Ecomate, because of its excellent solubility for all foam raw materials, was selected because it was envisioned as a potential softener for these MDI based products. They found that ecomate afforded very easy processability: They could use room temperature molds because of the lower boiling point of ecomate. In addition, they found they could demold foams much faster than previously because of the higher functionality of the isocyanate blend used.

Figure 4: MDI Pillow [left] and TDI pillow [right]

Of course, using MDI they shifted their index lower [using two or more polyols] to offset its increased functionality. The result was foam with very soft touch. As an adjunct to the lowering the foam index, the already lower cost of the isocyanate used made these products even more economical. These foams are snow white, and have all the properties previously obtained, with faster demolds, better hand, and best of all be more economical and more environmentally benign.

These ecomate-blown, MDI –based pillows are currently being sold in a variety of formulations – from Latex imitations, to very low density, to visco-elastic varieties. While a picture is worth a thousand words, it cannot adequately describe the softness and hand of these foams. Therefore we are bringing samples with us to the show. This company is thrilled with the results of the transformation, not only from an economic stance but because it is better for their workers and better for the environment.

We encourage you to investigate the same steps with your formulations.