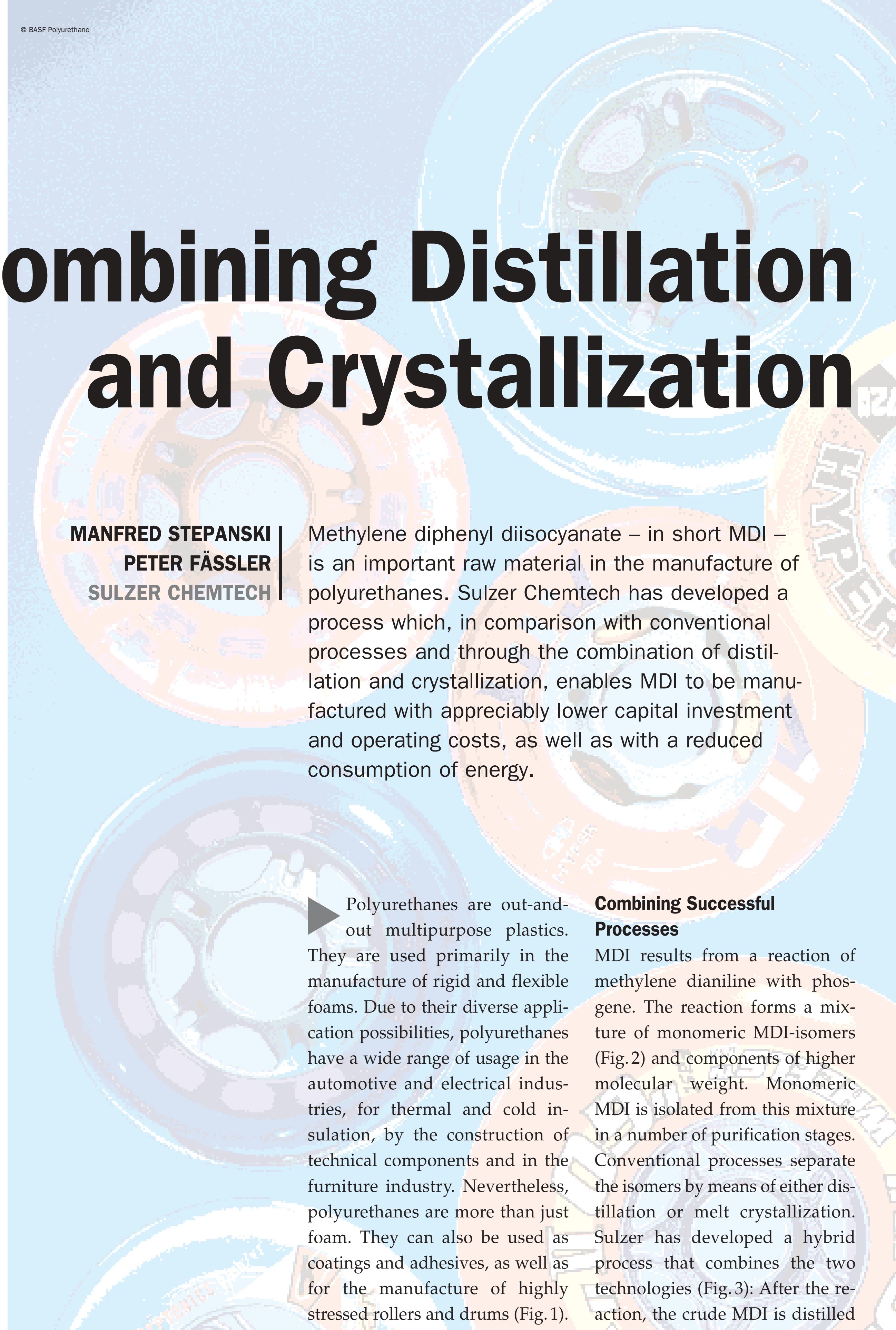

Combining Distillation and Crystallization

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Methylene diphenyl diisocyanate – in short MDI – is an important raw material in the manufacture of polyurethanes. Sulzer Chemtech has developed a process which, in comparison with conventional processes and through the combination of distillation and crystallization, enables MDI to be manufactured with appreciably lower capital investment and operating costs, as well as with a reduced consumption of energy.

Polyurethanes are out-and-out multipurpose plastics. They are used primarily in the manufacture of rigid and flexible foams. Due to their diverse application possibilities, polyurethanes have a wide range of usage in the automotive and electrical industries, for thermal and cold insulation, by the construction of technical components and in the furniture industry. Nevertheless, polyurethanes are more than just foam. They can also be used as coatings and adhesives, as well as for the manufacture of highly stressed rollers and drums (Fig. 1).

Combining Successful Processes

MDI results from a reaction of methylene dianiline with phosgene. The reaction forms a mixture of monomeric MDI-isomers (Fig. 2) and components of higher molecular weight. Monomeric MDI is isolated from this mixture in a number of purification stages. Conventional processes separate the isomers by means of either distillation or melt crystallization. Sulzer has developed a hybrid process that combines the two technologies (Fig. 3): After the reaction, the crude MDI is distilled

1 The majority of the wheels for in-line skates, microscooters or kickboards are made of polyurethane. Their manufacture requires MDI, which can be brought to the necessary purity with a Sulzer Chemtech process.

first to remove higher-boiling contaminants and readily volatile components. A product with more than 60% 2,4'-MDI and a pre-concentrated 4,4'-MDI are obtained in the isomeric distillation unit. The 4,4'-MDI is then concentrated to a purity of more than 99% in the downstream static melt crystallization unit.

Distillation with Low Pressure Drop

Successful Sulzer technology is employed in all process stages. The distillation column for crude MDI is equipped with flow-optimized MellapakPlus packings, facilitating high product throughput with exceptionally low pressure drop and lower hold-up of the liquid phase (see also STR 3/1999, p. 24, as well as the advertisement on the back cover of this issue). As a result of direct condensation, the distilled MDI is quickly cooled to storage temperature or processed further directly in the isomeric rectification column. The very short residence time at high temperature ensures smooth distillation.

High Throughput and High Yield

The distillation unit for the isomeric separation consists of a fractionating column with three or four beds equipped with highly efficient structured packings. The design criterion for the whole system is low pressure drop and minimum residence times. Thanks to the high throughput quantities, one distillation column is sufficient for large processing units having capacities of up to 160 000 tons per year, whereas two columns would be necessary with the application of conventional technology.
The not readily volatile bottom fractions from the two distillation stages are a marketable product with a high proportion of MDI-polymers. Residual monomers are separated from the bottom product in the recycling unit and returned to the distillation process again. With this step, the yield of MDI-monomers is markedly increased.

Separation without Solvent

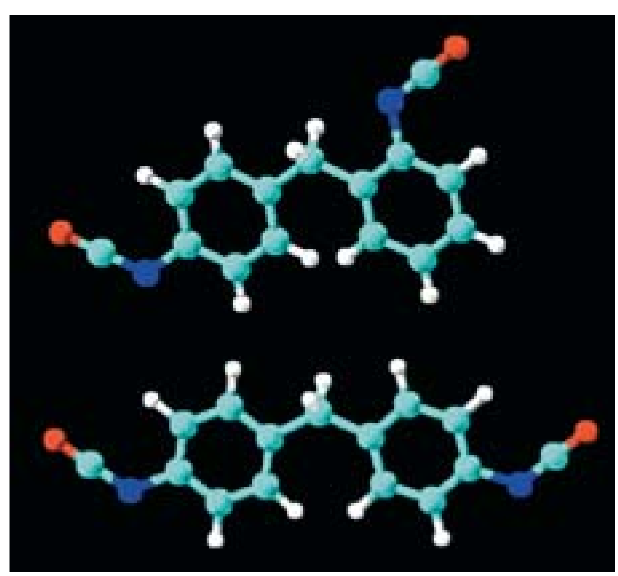
The pre-concentrated 4,4'-MDI from the isomeric distillation unit is routed continuously to the melt crystallization unit (see also STR 2/2002, p. 6). In this step, the feed product is crystallized by means of cyclic cooling and heating to separate polymers or other isomers. Static melt crystallization ensures excellent product quality and high color stability of the 4,4'-MDI-isomer. The process is very robust, since no equipment with moving parts is used, except for standard pumps and valves. At the same time, it is so flexible that the composition of the end product can be tailor-made to meet specific product requirements by control of the cooling and heating cycles (Fig. 4).

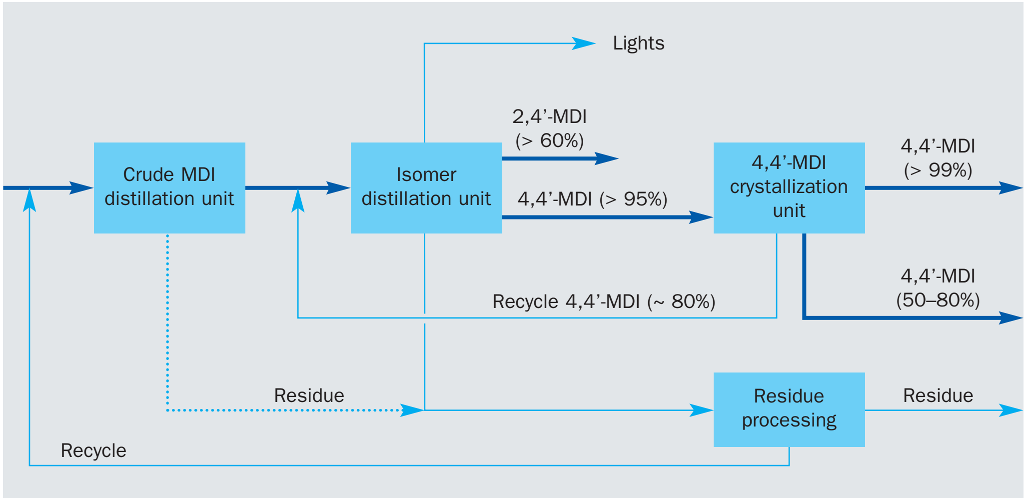
Scale-up in Large Plants

Sulzer Chemtech has conducted numerous pilot tests for the design of this new process on a large industrial scale. These tests for MDI-distillation cannot answer all questions concerning the behavior of participant substances. Sulzer Chemtech, however, has acquired decade-long experience with the distillation and crystallization of MDI in large-scale plants and can therefore exclude almost any scale-up uncertainty by the trans-

2 Isomers are chemical compounds, which are composed of the same kind and number of atoms, but have different physical or chemical properties. In the figure: 2,4'-MDI (above) and 4,4'-MDI (below).

Chemical Elements:
C N O H





3 Flow of material by the new hybrid process for the purification and separation of MDI-isomers. If one of the process units is already available in an existing plant, the capacity can be expanded by means of a retrofit.

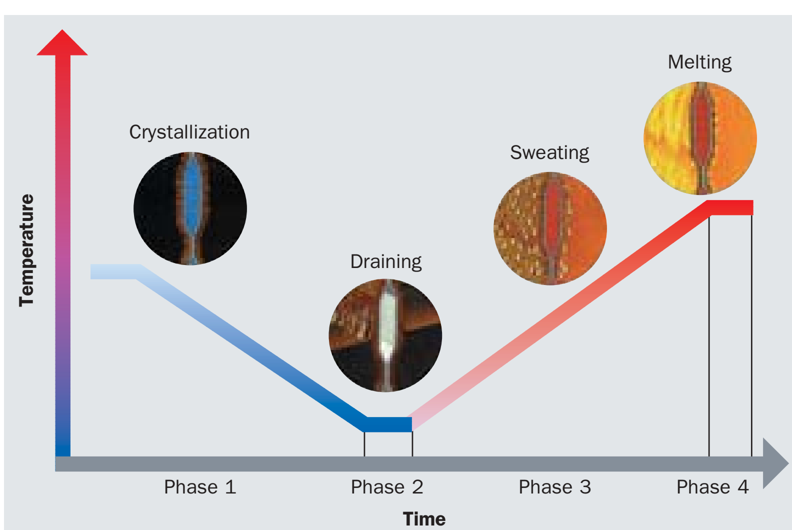
fer of test results to a large plant. Feedback from industrial practice and numerous reports from pilot tests facilitate process simulations for a wide spectrum of possible feedstocks. With this experience, plant design can be adapted very accurately and reliably to the customer's specifications.

The worldwide capacity for MDI is about 3.1 million tons per year and rising with annual rates of 4 to 5%. The new hybrid process from Sulzer Chemtech will have an important role in this market. The first contract has been received from Asia with the plant to be commissioned in mid-2003.

Further Fields of Application

The combination of distillation and crystallization not only enables producers to utilize the advantages of the respective separation process to the full, but also eliminates the disadvantages. The results are good yields with high product purity. High flexibility enables purity to be adapted easily to market demands. In comparison with conventional processes, optimized interfacing of components and goal-oriented control of the heat flows in the plant reduce consumption of high-pressure steam, cooling water, and electricity. And since the columns are equipped with highly efficient internals, the plant size needed for a specific performance is reduced along with decreases in capital investment costs for new plants. These advantages will bring Sulzer Chemtech further application potential in numerous branches of the organic chemical industry, especially where stringent requirements on product quality and low energy demand exist.

4 A product purity of more than 99.5% is realized in the crystallization stage. Any desired purity of the 4,4'-MDI can be achieved through further sweating or by repeating the whole cycle.



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