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ONE MORE TIME...
MORE DIFFICULTY INVOLVED...

MDI Processing Hints for Optimum Results

Presented by

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DEDICATED TO:

Bob Conn and Earl Butler, who, as working foremen at Thombert,Inc. have made quality MDI polyurethane parts for 29 & 35 years respectively.

One more time... More difficulty...MDI processing hints for optimum results.

TDI/Moca users have been spoiled by an isocyanate/curative relationship so convenient that users would rather fight than switch. Many processors have tried to switch from TDI to MDI and have found product quality problems due to the difficult processing characteristics of MDI elastomers. However, those who have religion; who truly believe it can be done...have mastered the chemistry and processing sensitivity of MDI systems.

The basis for these processing difficulties lies within the differences between MDI and TDI molecules. TDI has an NCO group in either isomer [2,4 or 2,6] that is sterically hindered. The arrangement of the NCO atoms in close proximity to each other hinders their reactivity. Consequently, TDI based prepolymers must be cured with a chemically aggressive curative, such as Moca. While many substitutes have been developed for Moca; most substitutes are still members of the same chemical family: aromatic amines.

MDI chemistry features an unhindered NCO on opposite ends of a linear double ring molecule. The high reactivity of this isocyanate allows formulation flexibility among a variety of chemically less aggressive diols and triols. The high reactivity of MDI and the formulation flexibility increase the difficulty in handling materials. This paper will share some practical processing tips from manufacturing experience at Thombert, Inc., a molder of MDI elastomers since 1958.

While MDI prepolymers have the lowest vapor pressure of all common isocyanate systems used in the cast industry and 1,4 butanediol (1,4Bd) and Hydroquinone Di(B-Hydroxyethyl) ether (HQEE) are non- hazardous chemicals, MDI is still an isocyanate and a known respiratory irritant. Moreover, it is often processed at high temperatures required to keep HQEE in solution and shrinkage under control. Basic principals of local exhaust ventilation should be heeded, including:

* Air flow should pass by employees before it reaches open molds, tanks, mix heads, and then into exhausters. One hundred feet per minute is considered adequate air flow.

* Sufficient air flow should be exhausted to remove prepolymers vapors from the work area.

* Containers with prepolymer should be covered when transferred or moved.

* MDI vapor is heavier than air and may tend to drift down but it is frequently used in the vicinity of hot air updrafts from ovens and hot plates. Horizontal air flow over the work area and into exhaust ventilation affords the best protection for employees.

Spills should be neutralized with a solution of ammonia and water and then cleaned up immediately. Curing ovens should be ventilated to the outside of the work area. Extra ventilation behind the cured parts in an oven should activate when doors are opened to assure that isocyanate vapors do not pass by the breathing zone of an employee.

If you exhaust various plant devices into a central plenum the collecting duct should have an exhaust that will maintain lower air pressure inside the exhaust system than in the work area. Thombert uses a variable speed drive on one exhaust fan which is controlled by the barometric pressure inside the exhaust duct to assure adequate exhaust suction.

MDI prepolymers, due to their unhindered reactivity, are very sensitive to heat and age. Ordinary preheat procedures which may have been acceptable for TDI prepolymers will damage MDI materials. Three days of preheating at 55°C in a recirculating convection oven is recommended as the best way to preheat prepolymers. Electric drum melters are second best and drum heating bands are worst for preheating. If you must melt a drum in a hurry, put it in a hot oven on a drum roller. Three days of heat exposure at 80°C will reduce free NCO by one-tenth of one percent, enough to cause significant stoichiometric change and drive physical properties far off specifications. If you suspect that a portion of a drum has been exposed to high temperature, vigorous mixing will disperse the damaged material and mitigate the change in free NCO.

If you have the capacity to measure free NCO, you should recheck any suspect material for damage. You may send a sample back to your supplier for NCO analysis if you don't have this capability. The following table shows how long MDI materials may safely be stored at elevated temperature with no risk of damage:

25° C	Twelve Months
60° C	Four weeks
90° C	Twelve Hours
105° C	Three Hours

These storage times are not cumulative and the % of each level that a material experiences must be added together...not to exceed 100% for assured safety.

Most material damage in a processors plant results from storage overnight or over weekends at elevated temperature. A day tank left at 90°C overnight or very hot spots (above 120°C) on a processing machine are dangerous. If your cure with HQEE which melts at 110°C you must run MDI systems very hot which increases the likelihood of a short term prepolymer temperature over exposure. The delays caused when an HQEE line freezes up [which is likely] are almost always fatal.

Processors who machine mix materials with on-the-fly degassers and large volumes of thru put are the most likely to have uneventful trials of MDI prepolymers. Right sizing the batch of prepolymer for a trial will avoid reheating materials which also adds to the heat history and affects quality.

Besides heat history, moisture contamination is a difficulty...particularly if you live in the 95% humidity zone part of the year. 1,4 Bd, TMP, and prepolymers are all hygroscopic and must be handled carefully. An air conditioned humidity controlled room is the best way to keep moisture away from chemicals. Blanketing process chemicals in day tanks with dry nitrogen is also an excellent control measure. Nitrogen, which is heavier than air, will act as a blanket andinhibit moisture contamination from atmosphere as tanks are opened and closed. Dry air systems that are rated at -40°F dew point will also offer protection, but are not effective as blanketing agents. Do not pressurize a tank with any gas that has not had moisture removed. HQEE due to its high melt temperature will boil moisture contamination away when liquid. Finally develop special containers for catalysts, colors, etc. that preclude moisture contamination. Often, the source of moisture is unsuspected and since the $NCO+H_2O=CO2$ reaction proceeds more readily with MDI than TDI, acceptable practices that work with one system may be marginal with the other.

One of the only areas where MDI and TDI behave in a similar manner is the selection of prepolymer backbones. Polyesters still provide dynamically tough elastomers with high tear strength, tensile strength, and sliding abrasion resistance. They are preferred for wheels, rollers, power transmission couplings, chopper cots, rotary die cutting pads, and snow plow blades. Polyethers are preferred for moisture and microbe resistance, high rebound, and impact abrasion resistance. They are preferred for water main valve coatings, pump impellers, linings, and skate wheels. Many parts can be molded of either backbone with successful results. While TDI esters have exhibited hydrolytic stability problems, MDI esters will be more resistant to degradation from water. Staboxol may be added to a curative when processed to further retard hydrolytic deterioration in esters.

When MDI elastomers are formulated, careful attention must be paid to the selection of curatives which may have to be blended to achieve optimum results. Trimethylol Propane (TMP) is frequently added to a curative in small quantities to improve the green strength of a fresh casting. TMP also improves the dynamic fatigue properties, the chemical resistance, and permanent set properties of the finished products. Catalysts or processing at higher temperature frequently improve the green strength of freshly cast components. They also decrease the mold residence time. Keep in mind that while higher chemical temperatures are the best catalysts, they post the most risk of damage to the prepolymer due to excessive heat.

Systems cured with 1,4 Bd should be cast at 97% stoichiometry. Those cured the HQEE should be cast at 90% stoichiometry. Processing ratios are extremely important when casting MDI elastomers, particularly those cured with 1,4 Bd. The following tables show that tear strength, tensile strength, and compression set all depend, to a large extent, on the stoichiometry. Hardness and reactivity do not vary with ratio and are not good indicators of processing errors. Only frequent calibrations of all equipment can avoid stoichiometric problems.

The enclosedphysical property tables, [See table I], show that only a two- or three-percent processing error within the already small portion of 1,4 Bd curative may change critical properties by as much as 25%. Many processors use split tear tests to evaluate finished elastomers as it is the most ratio-sensitive physical property, but a combination of tests tells the whole story.

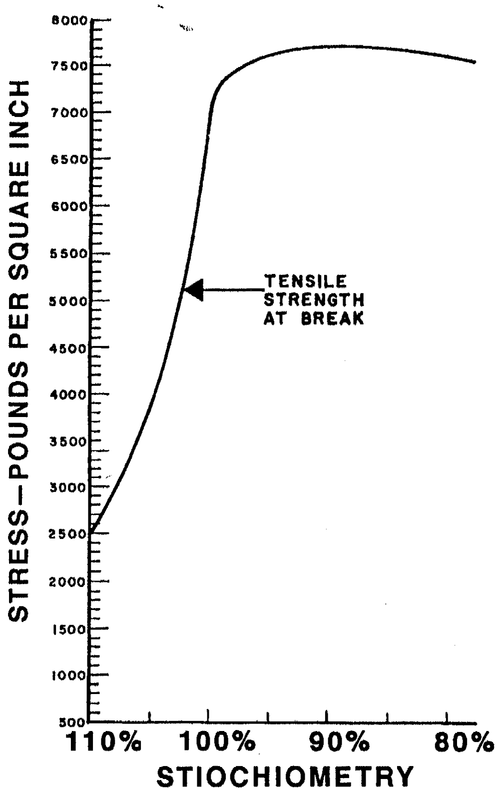
A low tensile test points to processing at 100%+ stoichiometry (see tensile strength curve). Tensile tests meet specifications from 80% to 99% stoichiometry. Tensile and tear tests taken together will indicate whether a processing error is positive or negative. Low tear and low tensile indicates 103%+ stoichiometry. High tensile and low tear strength indicates 94% or lower stoichiometry. Compression set may be used in lieu of tensile strength to evaluate stoichiometry.

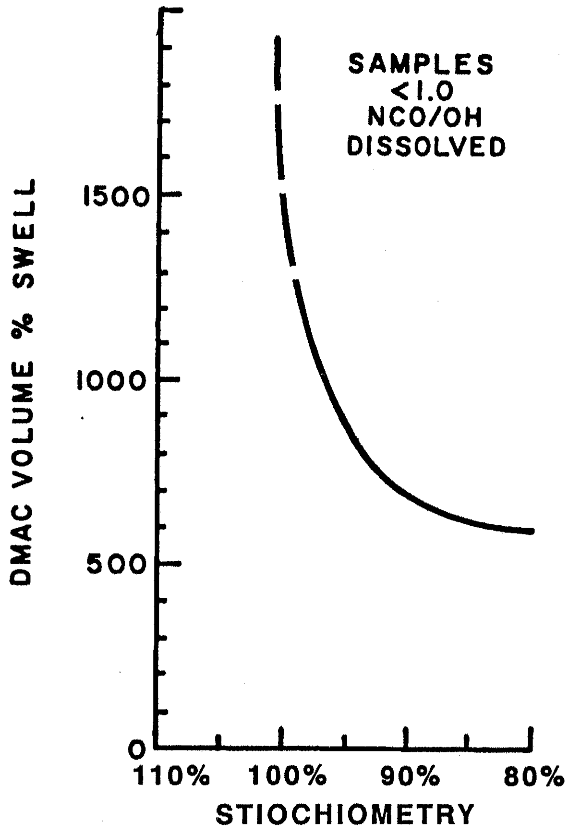
Another quality control indicator for finished elastomer is the dimethylacitamid (DMA) swell test. A 1" x 1" x 1/8" sample cut from a casting is immersed overnight in a petri dish filled with DMA. 24 hours later the sample is measured, its volume computed, and the percent increase is plotted against a curve to indicate the approximate stoichiometry.

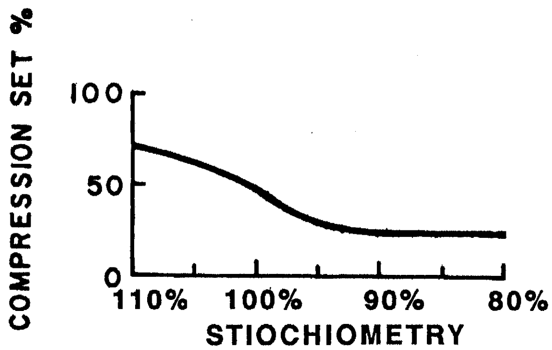
Hand mixing of MDI materials requires one minute of vigorous agitation for batches smaller than 1000 grams. Larger batches will require up to two minutes of agitation. Inadequate mixing may result in cracks, fissures, or lines, particularly in larger castings.

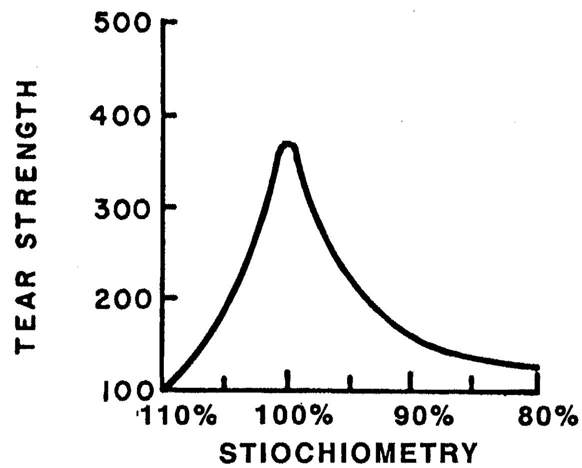
TABLE 1

TYPICAL PROPERTIES OF M-22
ELASTOMERS CURED WITH XB AT VARIOUS STIOCHIOMETRY









High shear mixing and metering machines are the most efficient way to prepare MDI elastomers. Air entrapment is eliminated and improved mechanical efficiency allows prepolymer temperature to be reduced to 95°C resulting in less heat history. Thombert, Inc. prefers gear pump machines with continuous flow. Our most recent machine includes recirculation and mass flow control for discrete shot dispensing. This type of machine, which is commercially available, offers the most flexibility with regard to pour speed and part size while maintaining accurate metering. We also prefer the slinger type degasser which seems to be the simplest on-the-fly degasser commercially available. Maintenance expense at Thombert, Inc. runs about one hour for every hour of machine operation. Much of our maintenance is scheduled preventive maintenance to facilitate continuous operation during production.

If flow control isn't available, stoichiometric changes will occur due to pump slippage, temperature related density changes, and back pressure change as pour speed is increased or decreased. Material buildup in the hose or mix head will also gradually change back pressure on the pumps. High maintenance of mixing and metering pumps minimizes this problem. Calibration of mixing and metering machines must take place with the machine operating at typical production speeds and material temperatures to assure accurate processing ratio. Tensile, tear strength, DMA swell, and compression set tests will help a processor trouble shoot their equipment.

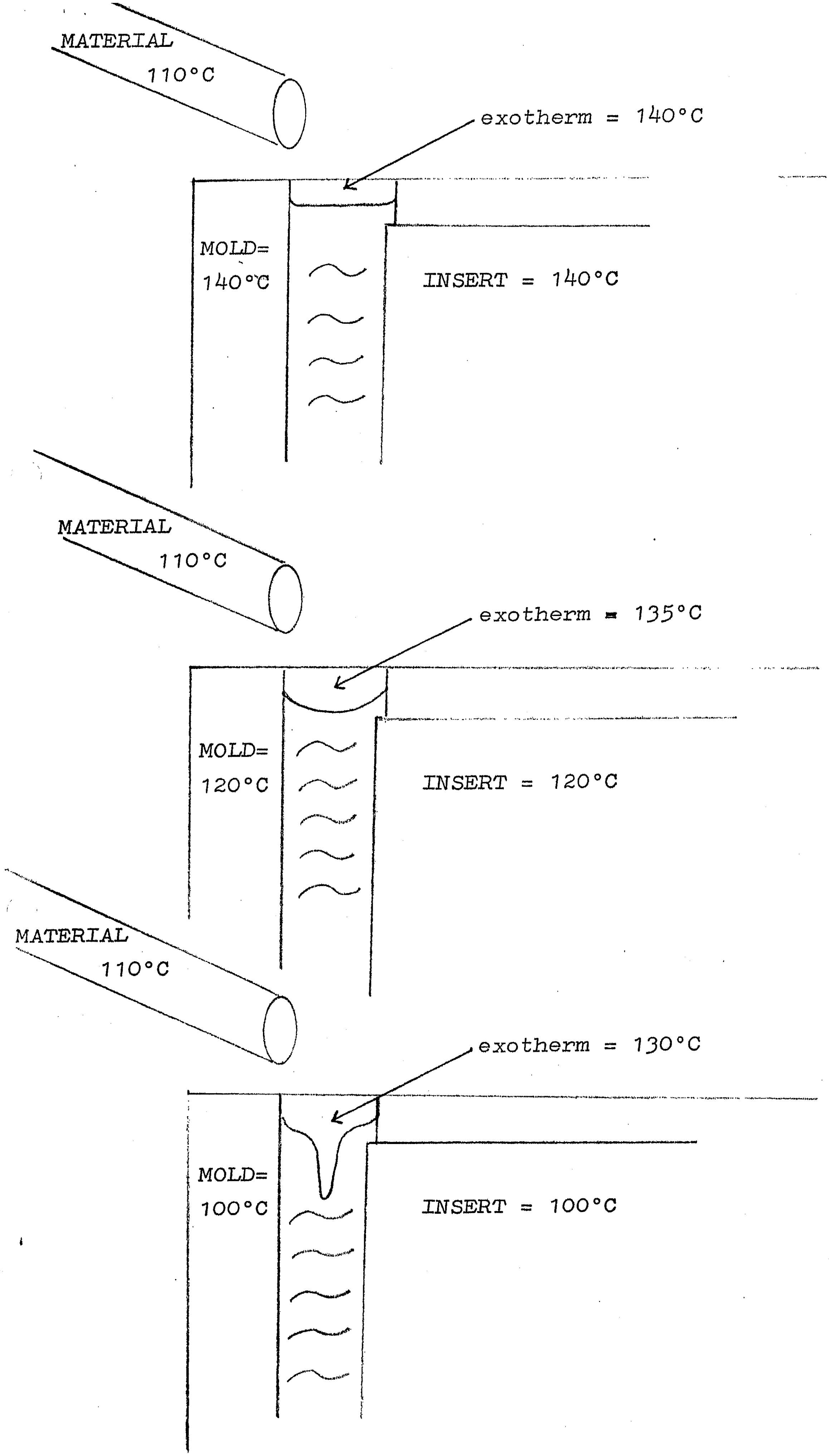
Several other steps help improve stoichiometric accuracy. Calibration stations equipped with micro processors which calculate exact weights for specific formulas and NCO% improve accuracy. If you use color additives, check to be sure the carrier (often DEG) is not reactive. If it is, compensate for it. A program to select the closest gear and pump combinations will eliminate guess work in setting up a mechanical pump linkage.

Thombert, Inc. has built machines with DC drive pumps equipped with RPM counters. The RPM counters feed back to a DC drive controller which divides voltage between multiple pumps. The machine is calibrated by dialing a new division into each pump. The drive control features a "ramping feedback" which assures that all pumps are in sync as volume of thru put is increased or decreased. As the drive control constantly monitors RPM from each pump, line occlusions or pump speed changes due to back pressure will be compensated for. This system, however, does not compensate for material temperature and density changes.

The ability to dial in ratio lets a processor test material stoichiometric levels to optimize a specific sensitive property, such as tear strength, which correlates with abrasion resistance.

MDI elastomers pass through a green stage when they gel which presents difficult shrinkage problems to processors. Freshly gelled elastomers do not have split tear strength or tensile strength as fresh TDI/Moca cured elastomers do. Splits, fissures, voids, and sink holes will develop if all temperatures are not accurately controlled.

To minimize these problems, a processor should strive to match mold and insert temperatures to the exotherm temperature of the chemical system at gel time. If the chemicals are hotter than the mold at gel time, the heat sink of the insert and mold along with the insulative properties of the polyurethane will cause a thermoplastic hot spot in the center of the casting. Shrinkage at this time will concentrate in the thermoplastic hot spot forming


MATERIAL
110°C
exotherm = 140°C
MOLD=
140°C
INSERT = 140°C
MATERIAL
110°C
exotherm = 135°C
MOLD=
120°C
INSERT = 120°C
MATERIAL
110°C
exotherm = 130°C
MOLD=
100°C
INSERT = 100°C

a sink hole and often a split or fissure in the nearby cooler portion of the casting [See Chart II]. Loss of catalyst potency or inadequate agitation of the curative /catalyst mixture can cause exotherm to vary. Handling conditions of chemicals prior to mixing, will vary exotherm if they are added to day tanks at different temperatures from the existing materials in the tank. As a general rule, molds and inserts should be hotter rather than colder than exotherm if you can't control temperatures exactly. This can result in mold and insert temperatures near 130-150°C which may then boil gases out of inadequately degassed prepolymer.

I consider mold and insert temperature issues so important to good MDI casting that I invest capital in massive convection ovens to maintain mold temperature. One million BTU capacity is necessary for a large tire oven at Thombert. Hot plates at best will lose 5°C for each inch of height over the surface with a steel mold. The necessity to provide 100 feet per minute ventilation across the surface of the hot plate aggravates this condition and covers are needed to prevent heat from escaping. Large molds and inserts should always be checked and ,if necessary, individually heated with a torch to achieve the proper temperature.

I also provide additional "double check" controls on temperature, including an infrared mold temperature sensor and dual oven temperature sensors. These sensors are connected to an audible alarm to prevent casting reject parts and wasted material. Mold temperature limits are ± 3° C.

Fresh cast MDI components should be protected from cooling after they are demolded. If they cool, thermal shock may inhibit curing of the finished casting. Castings should be placed in a curing oven for sixteen to twenty-four hours at 110°C. Adequate air flow around the curing parts is essential. After removing parts from the oven, an additional seven days of maturing is required before testing. This post cure period allows allophante bonding to take place.

Catalyzation and curing differences produce subtle changes in the finished elastomer that may not be evident for thirty days. This is particularly true of large castings. Catalyzed elastomers exhibit less chemical and solvent resistance and lower tensile modulous but higher dynamic performance due to the cross-linked network. Compression set is raised Many very important processing hints have been enumerated in this article. However the most important element of successful MDI processing is the issue of commitment. Very careful attention to detail is required if you are to be a successful processor of these materials. A constant quest for process improvements has helped Thombert, Inc. remain competitive in many different product lines during our thirty-five year polyurethane processing history. Hydrocyclones, bowling balls, recoil dampeners, flexible couplings, wheels and tires, valve inserts, pipeline pigs, large rolls, rotary die cut rolls, wear resistant sheets, grain elevator buckets, snow plow blades, and salt/sand spinners along with many other components have been successfully cast from MDI elastomers.

Firms contemplating a switch to this chemistry have an excellent chance of success if they commit to review all aspects of their process with these guidelines in mind. Comparable quality to TDI/Moca systems is achievable; there is simply more difficulty involved.