AN ALTERNATIVE TO TDI-PREPOLYMER/MOCA TECHNOLOGY:

PLAN B

A PATH TO FEWER REGULATIONS

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Introduction:

There is nothing wrong with the TDI-Prepolymer/MOCA technology. It was first commercialized in the 1950’s and since then the technology has grown both in the length, depth and scope of application. Initially regarded as a space age elastomer used only in very special, yet limited applications where cost was of secondary concern to a widely applied material in all sorts of size, shape and durometers. Over the years the technology has grown and expanded to include a wide variety of polyol types, polyol molecular weights, polyol functionality, polyol blends as well as different isomer blends of TDI.

Paired with MOCA; the chain extender or curing agent, TDI-prepolymers had many advantages such as:

Less sensitivity to ratio

Less sensitivity to moisture

Easy to mix-MOCA super cools and is very soluble in prepolymer

Reasonable pot lives, making it possible to hand cast or machine pour intricate or large parts
Smooth polymerization, cracking and debonding from substrates is minimized.

Outstanding wide ranging physical properties of the resulting vulcanizate.

Of course there has been for many years attempts to find an aromatic diamine that could replace MOCA. There are many replacement aromatic diamine candidates for MOCA with a wide variety of melting points, solubility parameters, processing limitations and of course, cost. The most successful one, to date that is commercially available that meets many technical demands and criteria of regulators, processors and end users is dimethyl thiotoluenediamine, commonly known as Ethacure 300 or E-300.

It was a long, hard and costly process that the manufacturer had to go through to get this chemical approved for use in our industry. Yet one has to ponder if, in the future, regulators will target Ethacure 300 in a similar matter as they did MOCA. If so, this means more regulations, more testing, more paper work, more cost. This process could go on for years without any final resolution. It seems that the regulators just do not like aromatic amines, no matter how useful and beneficial they are to society, to be used in industry, especially by small companies.
To further complicate matters, the American Conference of Governmental Industrial Hygienists (ACGIH) has just voted to adopt new (lower) time-weighted average (TWA), short-term exposure limit (STEL) and threshold limit values (TLVs) for all isomers and isomer blends of TDI. Specifically as of February 1, 2016 the new values are:

TLV-TWA (8-hour TWA) from 5 ppb to 1 ppb

TLV- STEL (15-min TWA) from 20 ppb to 5ppb.

These are, of course, voluntary standards. However, if history offers any guidance, ACGIH standards are usually quickly adopted by state and federal regulatory agencies.

Reliable, accurate and repeatable measurement of anything in the parts per billion (ppb) range is very challenging. Complying with numerical standards depends upon accurate measurements: and will not doubt lead to costly legal defense by TDI prepolymer processors.

Looking a bit into the future, it is reasonable to assume the TDI prepolymer/ MOCA technology is being attacked from both sides by regulators: TDI and MOCA.
An Option:

If this scenario, outlined above holds; what can our industry, typified by small, entrepreneurial businesses do about this distributing trend, given our limited technical and financial resources?

One possible solution is the combination of vortex mixing and MDI based one-shot technologies. This concept unites the physics of intimately mixing materials (multiple liquids and/or liquids and solids) and MDI chemistry.

Vortex mixing is a very clever way of mixing two or more liquids together. Solid matter can be mixed in also. Simply explained, the materials are weighed out and put into a special plastic container, sealed and placed into the machine. The vortex mixer rotates in two dimensions, creating a complex shearing action. The liquids or liquids and solid particles are quickly and intimately mixed together with little or no entrained
gas. The machine is then stopped and the mixing container removed and the contents poured into molds. The mixing container then can be cleaned and reused.

This concept fits very nicely for small to medium size processors. They could be classified as a job shop-juggling many customers with small to medium size order volume, many material and color changes.

So much for the mixing phase. Let’s talk about the MDI chemistry. Pure 4,4′-MDI, as many of you know, is hard to store because it tends to easily form dimer and cannot be stored at room temperature. It is also a solid at room temperature and must be carefully melted before being put into process. Any prepolymer made 4,4′-MDI also is subject to dimerization. The rule of thumb with any 4,4′-MDI prepolymer is to consume it as soon as possible with as little of exposure to heat (heat history) as possible. It is not too much of an exaggeration to say “Time waits for no man or 4,4′-MDI”.

All is not lost! There is a clever way to minimize the dimer problem. 4,4′-MDI can be modified to greatly reduce dimer formation even to the point where it can be stored at room temperature for long periods of time with minimal dimer formation. There a few ways to do this: uretonimine modified 4,4′-MDI seems to stand out
as the most practical. They are also liquids at room temperature. These two characteristics are extremely important when it comes to the practical production of cast parts by vortex mixing of one shot urethane processing technology.

The Chemistry:

One-shot urethane chemistry is, in principle, very simple. Monomers of the isocyanate ("A" side) and polyol side ("B side) are mixed together all at once. There are no prepolymermixes involved. Pure TDI is never considered in this process because of obvious serious safety concerns.

There are some limitations to this chemistry, of course. One has to be aware of the possibility of excessive exotherm and precipitation reactions. Precipitation reactions occur when too much short chain diols such as ethylene glycol or 1,4-butane diol are incorporated into the formulation. These precipitants are in the form of tiny, white insoluble crystal-like particles which ruin the elastomer. These are not insurmountable problems but should be considered boundaries of this technology. All technologies have boundaries.

By working with only monomers, a whole new world of possibilities opens up. The urethane processor can
purchase a very limited amount of monomeric raw materials and make a vast array of urethane elastomers that meet most end user requirements—now met by prepolymer technology. With a little experimentation, trolling the internet for old patents and references to technical/trade journal, the PMA’s Virtual Technical Library and past technical papers as well as tapping the knowledge of technical experts at key raw material suppliers, you too can master this technology to your benefit. And, of course, your fellow PMA members, especially the “old guys” are an excellent resource. Remember, one-shot and quasi-prepolymer technology has been around for 50+ years and is no longer considered rocket science.
Discussion:

Let’s take a minute to review some of the advantages and possibilities of combining vortex mixing with one-shot urethane processing technology.

Blended Polyols: By utilizing various molecular weight polyols, unique properties can be optimized. Examples are blending very high molecular weight diols such as a 4000 mw PPG with a short chain glycol such as diethylene glycol (DEG) or dipropylene glycol (DPG) results in unexpected optimization of elongation, rebound and tear resistance. Another variation of this blended polyol strategy is to blend high, medium and low molecular weight polyols with the objective of more evenly distributing stress as a urethane component is in service.

Another practical consideration is blending PPG triols with diols-again with different molecular weights to meet end-use requirements.
Still another practical consideration is blending PTMEG/PPG polyols; again with the same or different molecular weights and functionalities.

Mixed Polyols: The literature is full of articles and patents detailing the benefits of blending carefully selected polyether and polyester polyols to enhance certain specific physical properties. Here again is another avenue to explore to get what you require to meet an end-use demand.

Compatibilizers: There are number of suppliers of specialty chemicals that enable incompatible combinations of desirable components to become homogenous, making processing the impossible to be a routine matter.

Catalysts: Most likely some sort of catalyzation will be required to make many of these systems to be practical. With respect to choice of catalyst, the processor is no longer limited to a few so-called standards like dibutyl tin dilaurate and triethylenediamine. There are scores of others available, each with its own unique reaction profiles. There are even delayed action catalysts as well as inhibitors such as benzotriazole. Benzotriazole has been documented to slow down (inhibit) very high NCO and hence very fast urethane systems to the point where they can be processed in a shop environment.
Fillers: Adding solid fillers to a cast urethane processed through a dispensing machine is almost impossible. Pumps, flow meters, mix head, orifices and even holding tanks are easily plugged or damaged. In short, it is just not practical.

By using a vortex mixer, solids can be simply be added to the liquids and then mixed in as usual. In the worst case, the solid can be added to the “B” or polyol side first then the isocyanate be added as a second step.

The potential of adding solid materials to liquid castable urethane elastomers to improve their performance and/or reduce cost is exciting. You need not be limited to solid, inherit powers such as amorphous silica in the 10 to 20 micron particle range, commonly used in low durometers rollers. There are a host of other types of solid fillers commercially available: powers, fibers and palettes. Each of these shapes will contribute specific characteristics to the vulcanizate. These materials can be combined with special silanes or titanates that will chemically bond the inert filler to the urethane polymer
matrix (see PMA technical Papers # 63, 95). I can visualize many interesting, commercially important applications where this technology could be profitability applied.

Thixatropy: Take the case of the use of molybdenum disulfide (MoS2) added to urethane elastomers to reduce the coefficient of friction. Molybdenum disulfide has a high specific gravity and tends to quickly settle out in the mold before the rising viscosity (gel) can retard settlement. This phenomena makes it is difficult to pour parts with the MoS2 uniformly distributed though out the part. By using the vortex mixing/ one-shot technology the incorporation of carefully selected thixotropic agents, high specific gravity particle settlement can be controlled.

Organic Fillers: Cellulosic fillers, such as nut shell flour or particles are readily available and are cheap. They are loaded with hydroxyl groups just waiting to react with isocyanate in the mix. The result would be chemically bound, cheap filler. Nut shell flour and particles do contain moisture and can be tricky to sufficiently dry, but it can be done.

Moisture Control: Everyone knows that moisture can be a big problem, especially in MDI-based systems. Got a moisture problem? Just add a small amount of
molecular sieves to the “B” side and the problem usually is resolved. Molecular sieves are readily available in powder form or as dispersion in castor oil-based polyols.

Conclusions:

So there you have it- an alternative to TDI/ MOCA technology. I have presented a very large and varied list of possibilities of this technology. The objective is not to overwhelm the reader but to set forth a pathway that the average small to medium processor can survive in the post MOCA/ TDI prepolymer world, if that should come to pass.

Of course, nothing yet has been found to fully replace MOCA cured TDI prepolymerrs with respect to their performance, processability and cost. However, the industry may be forced to live with what is possible and practical under a new world order. A good example of this is story of asbestos. Asbestos fibers had over the course of more than a century found thousands of practical applications from brake pads to vinyl floor tile to concrete pipe to missle reentry nose cones. It is now banned but somehow industry and society have adjusted.
Let’s hope MOCA/ TDI prepolymer technology muddle on. But just in case it doesn’t, the industry needs a plan “B”.