FORMAT

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Applications for Authorisation

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TABLE OF CONTENTS

1. SUBMITTER'S INTERESTS

The Polyurethane Manufacturers Association ("PMA") is an international association representing cast elastomer polyurethane processors and suppliers, including companies which have a presence in and/or sell into the European Union ("EU"). PMA appreciates the opportunity to comment upon the application to authorize the use of MOCA as a chain extender and curing agent in the manufacture of polyurethane cast elastomers as MOCA and the implications of being limited to non-MOCA alternatives are vitally important to the operation of PMA members' facilities in the EU and in many countries outside of the EU.

2. GENERAL INFORMATION REGARDING ALTERNATIVES TO MOCA

Although a number of alternatives to MOCA have been developed and are available on the market for use in the production of polyurethane products and cast elastomers, a number of impediments exist to the wholesale substitution of MOCA in the castable polyurethane market. For example, given the structural differences of these curing agents and chain extenders to the structure of MOCA, processing with these alternatives requires significant changes in handling, equipment, and additional chemical usage (e.g., to extend pot life). The resulting products differ in performance characteristics and production costs.

3. TECHNICAL IMPACTS

Because the chemical structure of MOCA serves to slow the rate of reaction as compared to alternatives like MDA, the use of these alternatives results in a much shorter pot life – in some instances reducing pot life from 15 minutes to 0.1 minutes – or in exothermic reactions posing a work exposure hazard and affecting product quality. To adjust to these shorter processing windows, processors must either shift over from hand-batching operations to automated equipment or use other approaches to extend pot life (e.g., use of additional chemical additives) and address hazardous exothermic reactions. In addition, many MOCA alternatives are also less forgiving to even slight ratio variations and changes in moisture. Also, many non-MOCA formulations suffer cure too rapidly (not conducive to good bonding with substrates or resulting in tearing in the developing elastomer structure or failure at the bond line) or have much weaker green strength (leading to longer mold times, increased demolding difficulties, and product failures), all of which result in higher product failure rates, longer overall processing time, and increased production costs.

Formulation differences also result in differences in strength, abrasion resistance, temperature resistance, durability, and appearance of final products. While studies produced by manufactures of MOCA alternatives have shown that some products exhibit improved strength or abrasion resistance, their utility is limited by their higher sensitivity to temperature, moisture, slight variations in ratios, and presence of impurities. In addition, these studies do not provide long term durability information for the wide variety of cast elastomer products which are essential components and devices in consumer goods and commercial, industrial, and military equipment. Thus, the effective lifespan of non-MOCA derived products will not be known to cast elastomer processors or end users; the impact that this will have on end users' repair and maintenance schedules (and associated costs) is also uncertain, however, negative impacts on user confidence in the reliability of non-MOCA derived products are expected.

Because components in non-MOCA-based systems are not freely interchangeable, cast elastomer processors using non-MOCA formulations will be locked-in to the same source to ensure consistency in their final products. In contrast, MOCA is highly compatible with a

wide variety of TDI prepolymers (ethers, esters, caprolactones, carbonates, etc.) over a wide range of isocyanate percentages. This compatibility makes mixing much easier and predictable and resulting in fewer rejected parts, which is very important for small shops as many do a significant amount of hand-batching work. In addition, MOCA can maintain a cooler curing/reaction temperature; this is important for both hand-batching and machine processing cast urethane elastomers as lower curing/reaction temperatures allow for longer gel times, which is critical for pouring into molds for large or complex configurations.

4. ECONOMIC IMPACTS

In the absence of a robust data set regarding the long term durability and other performance characteristics of products formulated with these alternatives, the impact on end users' maintenance and repair schedules is uncertain. Costs associated with premature equipment failure (and, potentially, consequential damages) will have to be borne by product users or shared with (or shifted onto) processors.

To remain competitive with non-EU cast elastomer processors, EU-based processors must conduct research and development to identify appropriate substitutes which will yield products with performance characteristics similar to MOCA-produced goods for each individual application. The cost of these research and development efforts will have to be absorbed by or shared among cast elastomer processors, chemical suppliers, and their customers. So, too, higher prices for MOCA alternatives must either be borne by processors and their suppliers or passed on to their customers. PMA expects that industrial users will likely balk at the production premiums associated with more costly MOCA alternatives, which will result in processors having to absorb some of these increased costs. For some applications, PMA expects that end users will opt to reject materials produced with MOCA alternatives as unsuitable replacements or to purchase more inexpensive products from foreign suppliers in other non-EU countries.

5. CONCLUSION ON SUITABILITY & AVAILABILITY OF THE ALTERNATIVES

The adverse implications of not granting authorization for use of MOCA in the EU are not easily quantifiable; however, the competitive disadvantages to EU-based cast elastomer processors and potential performance problems posed to EU businesses supplying alternatives and consumers militate for its authorization. In addition to the known manufacturing and performance differences associated with cast elastomers made with MOCA alternatives, significant cost differences between MOCA and non-MOCA chain extenders and curing agents will likely cause end users to source their products from non-EU sources and for EU-based cast elastomer processors to close their operations or relocate outside the EU.

REFERENCES

I.R. Clemitson, Castable Polyurethane Elastomers, CRC Press (2nd ed. 2015)

Chuck Demarest, Life Beyond MOCA, Conference Paper, PMA Annual Meeting (May 2014)

Thomas Peter, et. al, Choosing the Best Alternatives to MOCA cured TDI Polyurethanes, Conference Paper, PMA Annual Meeting (May 2016)

APPENDIX A. COMPILATION OF PMA MEMBERS' COMMENTS ON MOCA ALTERNATIVES

MOCA Alternative	Performance Observations	Cost Information	Other Information
3,5-diamino-4-chlorobenzoacid isobutylester EC No 251-311-5, CAS No 32961-44-7	This product has been used for 30-40 years to replace MOCA. Some mechanical properties of articles produced with this replacement product are not as good as those produced with MOCA. Reactivity: Comparable to MOCA.	The price compared to MOCA is much too high (increased by a factor of 4).	Estimated market share is 1% of the world-wide market (MOCA = 100%).
Dimethylthiotoluenediamine (DMTDA) (isomers) EC No 403-240-8, CAS No 106264-79-3 (Commercial name: Ethacure 300)	This product has been used for decades to replace MOCA. The product is liquid at room temperature. Approximately 20% less product is needed; however, no cost savings are realized as the product is significantly more costly. Most of the mechanical properties of the products produced with DMTDA are not as good as MOCA-based products; also the aging properties (e.g. hydrolysis) are inferior. Also, pot life is 1-2 minutes shorter, with comparable demold times. DMTDA yields compression moldable products. Some PPG vulcanizates are not suitable for outdoor applications. Vulcanizates darken faster and more when exposed to sunlight/heat. Black pigment as well as UV/antioxidant packages (increases cost) can be used to improve color stability.	The price compared to MOCA is much too high (increased by a factor of 2 to 3 times). Some product has been priced at $5.50 - $7.50/lb., depending on volume and manufacturer.	Estimated market share is 5% of the world-wide market (MOCA = 100%). The product has an unpleasant, sulfurous smell. An advantage is that the product is liquid at ambient temperatures. However, in most applications the properties of the produced products are not sufficient to replace MOCA.

MOCA Alternative	Performance Observations	Cost Information	Other Information
	Reactivity: In most applications is too short compared to MOCA. It exhibits a slightly higher level of reactivity than MOCA and the end processor must consider this aspect.		
DETDA-80 (isomers) EC No 270-877-4; CAS No 68479-98-1	A theoretical alternative, as the reaction time is much too low for cast elastomer applications. It can be used in some reactive applications (rotational cast elastomers) <<< 1%.		
MCDEA EC No 402-130-7; CAS No 106246-33-7	This product has been used for years and provides products with better mechanical properties than MOCA. Reactivity: The reaction time is much too fast to process this amine in most applications.	About 6 times more expensive than MOCA	Today, this product is used in niche applications where high dynamic is needed, a high price can be paid, and a short reaction time can be accepted.
MDA CAS No 101-77-9	MDA is identified as a potential alternative due to its chemical structure being similar to that of MOCA. Reactivity: MDA is not suitable to replace MOCA due to faster reactivity in the application than MOCA.		MDA is not suitable to replace MOCA due to its higher toxicity.
Gantrade's functional diamine curatives – "A23X series"	They have fast curing options and slow curing options which would be good for hand-batchers. The data that is available suggests that properties can be tailored, based on the choice of curative	General price range is significantly higher than MOCA (~$13.00-$16.00/lb).	

MOCA Alternative	Performance Observations	Cost Information	Other Information
	grade.		
Use of MDI prepolymers	In general, the physical properties of MDI/BDO materials are lower than TDI/MOCA. In addition, it is very difficult to make large and/or complex parts using MDI/BDO systems. MDI/BDO systems are also particularly sensitive to variations and ratios must be controlled much more exactly than TDI/MOCA (TDI/MOCA is very forgiving, tolerating variations (over or under) of ~3%). This leads to issues in hand-batching. Some MDI's require much different handling of the materials including getting actual weights on the prepolymer, back calculating the amount of curative, and adding with a syringe on a scale to 0.01 grams to get the correct amount. Thus, most MDI processing is done with machines. Molding temperatures also need to be controlled more tightly to yield good parts. MDI/BDO systems have poor green strength leading to longer demold times. Green strength can be improved with catalysts but this lowers the pot life so that hand casting is not possible. Finally, some users have not been able to successfully compression mold MDI formulas. The gel curve of the TDI/MOCA is gentle enough to allow time to close the mold, get it in		

MOCA Alternative	Performance Observations	Cost Information	Other Information
	the press, and close the press. MDI systems tend to gel very quickly and not allow the time needed to get everything into the press and closed up.		