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IMPROVED RIM PROCESSING WITH SILICONE INTERNAL MOLD RELEASE TECHNOLOGY

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BACKGROUND OF THE RIM PROCESS

In 1974, the first commercial urethane part was molded by a newly developed process known as reaction injection molding or RIM. Today, RIM is a leading plastics process developed for high delivery and low rejection rates, thereby meeting current product design, production, and performance challenges. Reaction injection molding is defined as a plastics manufacturing process in which two reactive liquid chemicals are forced at high pressure to impinge mix in a small chamber and instantly dispense into a closed mold at relatively low molding pressure where part curing and solidification occurs. RIM gave the plastic manufacturer a new molding method with great tooling variety and process versatility. This has allowed RIM processing to maintain a healthy annual growth rate over the past several years [1].

Synonymous with RIM is the chief classification of elastomer that is currently being produced by reaction injection molding—namely, polyurethane. This material, as molded using RIM techniques, has advantages of excellent flexural strength, low weight and good dimensional stability with excellent chemical resistance. The largest current use of RIM produced polyurethane is automotive front and rear fascia.

MAJOR RIM DEVELOPMENTS

The cycle in a reaction injection molding process can be described by these six operations:

1. press movement,
2. cylinder pressurization,
3. injection,
4. curing,
5. part removal and
6. external mold release application.

Figure 1 represents the relative percentage of time that each of these operations consumes of the total RIM cycle. Data shown here were obtained during actual molding operations of a glycol-extended RIM system on an Admiral 9000 3HP machine equipped with an automotive fascia tool. This molding operation is typical of the cycle times seen with most current production RIM equipment.

An emphasis on "fast-cycling RIM" reduced cycle times from 340 seconds in 1974 to approximately 150 seconds by 1981 [1,2]. This represented a 55 percent reduction in overall cycle time. Much of the improvement in cycle time that has been seen during this time has developed from improvements in the injection and cure steps. Introduction of the fast cure amine extended systems [3] and today's faster reacting glycol systems have reduced polymerization cure time by an astounding 75 percent. These systems react and develop green strength faster, thus allowing for shorter cure time, expediting demolding. In addition, equipment modifications allow faster closing and opening of RIM clamps.

NEED FOR INTERNAL MOLD RELEASE

Efforts continue towards improvements and modifications for faster-curing chemistry and faster-moving equipment. In addition, much current interest is focused around improvements in the mold preparation operation in the RIM cycle.

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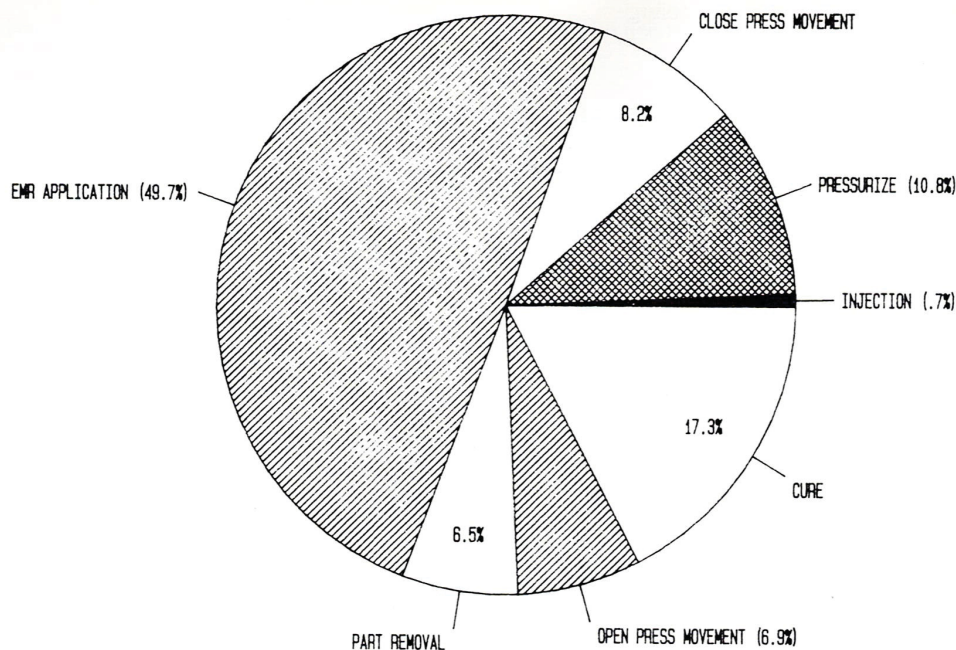


Figure 1. Typical RIM cycle measurements.

Presently, elastomeric polyurethane, molded using reaction injection molding techniques, must rely on the use of external mold release agents in order to facilitate part removal from the molds. These wax or fatty ester-soap based external mold release agents are typically applied before each part is made. This application step is extremely time and labor intensive. The application of external mold release agents can consume 25-50 percent of the RIM cycle depending on mold design and complexity of the molded part. An alternative to the present mold release situation is the development of *internal* mold release (IMR) agents which work in conjunction with external release agents. Such synergism allows the molder to produce multiple parts before the external release agent must be reapplied. In the industry this is frequently referred to as "multiple release from an external mold release basecoat." One mathematical model of the RIM process [2] suggests that the vast majority of the benefits of using IMR are realized by a system which allows a minimum of 20 parts to be molded before basecoat reapplication. However, future generations, including bare metal release, are being evaluated.

The use of IMR as an alternative to the reapplication of an external mold release agent has some significant economic advantages. With internal release, the cost of the external release agent will be reduced, as well as the time consumed during each cycle for application. Average improvements in cycle time of 38 percent have been observed [1,2,4]. Reduced cycle times mean less labor and utility cost per part. Productivity increases will also extend capacity

limits on existing equipment. This may delay or eliminate the need for further capital expenditure at that point in the future when demand exceeds current production capacity. In addition, the use of IMR technology will reduce the number of parts that must be rejected due to poor surface quality. Since less external mold release per mold cycle would be applied with IMR incorporation, part cleaning cost and mold stripping times will be reduced. Finally, reduced spraying of external mold release may improve air quality. All these result in overall improved operating efficiency of a RIM molding plant.

REQUIREMENTS OF AN INTERNAL RELEASE AGENT

For internal mold release to be a viable processing alternative, it must fulfill a number of demanding requirements:

Release

Rather obviously, the IMR must provide release.

Paintability

Of equal importance in automotive applications is the need to mold parts which are paintable after normal cleaning. Following standard cleaning and painting procedures, a painted part should pass aging in

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Reactivity

Faster processing of urethane systems has been obtained by improvements in the development of green strength or cure rate, allowing quicker part removal from the mold [3]. IMR additives should not significantly reduce reactivity. The effects that internal mold release agents might exhibit on the reactivity of a given RIM urethane system can be determined through measurement of the cream (gel) times of systems with and without the IMR.

Nucleation

Most elastomeric urethane systems are molded to a reduced density to lower cost, to allow complete mold filling which yields better surface quality, and to provide optimum physical properties. A microcellular structure is achieved by nucleating with a gas or incorporating a blowing agent. An internal release agent should not affect the cell structure or froth stability, as these could result in a change in physical properties.

Physical Property Retention

Another consideration with the use of internal mold release agents is that they should not adversely affect the performance of the finished part in its application. This can be tested for by comparing physical properties of parts molded with and without the internal release agent. No significant differences should be observed.

In the development of release agents for RIM molding, one or more of these requirements can appear to be in opposition with one another. Materials which might be excellent release additives become commercially ineffective because of a possible lack of paintability. Obviously, as the number of requirements increases, the number of fluids which meet all these requirements becomes limited.

ORGANIC-SILICONE HYBRID TECHNOLOGY

Current technology allows the synthesis of hybrid molecules that are part silicone and part organic. Materials can be designed that have the good release properties of a silicone combined with various types of organic reactivity. The ability to vary not only viscosity, but also the reactive group, and the number and position of reactive groups (i.e., AB, ABA, rake structures) allows an infinite possibility of materials and adds a unique dimension of versatility.

Examples of these structures are shown by the following formulas:

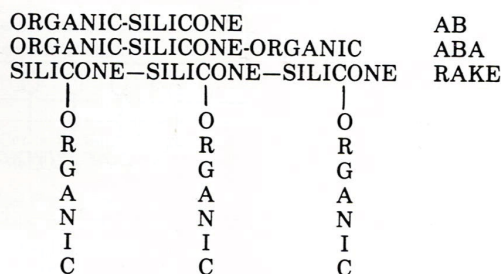


Figure 2 illustrates how the tailor-made silicones function as IMR agents in RIM molding. Due to the known surface tension reduction phenomenon of silicone fluids in urethanes and the differences in surface tension at the urethane/mold interface, internal mold release agents based upon silicone molecules can be developed to selectively migrate at different rates to the urethane/mold interface. There, it will orientate itself to build a protective layer which decreases the ability of the urethane to wet-out the mold surface. The inability of the urethane to wet-out the mold surface will facilitate release.

Although many fluids can be developed to act as IMR for RIM, many would fail as commercial products due to their inability to impart paintability to the resulting molded part. In order to rectify this paintability concern with the use of silicone internal mold release agents, a functional moiety is designed into the silicone. This functionality, when correctly specified, reacts into the urethane matrix once the IMR has migrated to the urethane/mold interface. This reactivity causes the IMR to be immobilized in the urethane matrix, thus allowing paintability.

Silicone organic hybrids play a critical role as surfactants in the formation of polyurethane foam [5]. These surfactants are tailored to provide the balance of reactivity and compatibility required for proper foam stabilization. Similarly, silicone fluids designed for RIM release must also adequately stabilize the cell structure of the faster RIM-processed polyurethanes.

FIRST SUCCESSFUL SILICONE-ORGANIC HYBRID IMR

Dow Corning has demonstrated the ability to use silicone technology for developing an internal mold release for polyurethane RIM by introducing DOW CORNING® Q2-7119 Fluid as the first IMR agent commercially available to the RIM industry. Field evaluations of DOW CORNING® Q2-7119 Fluid in amine and glycol extended systems demonstrated the ability of this functional silicone fluid to act as an internal release agent. Table 1 shows results of DOW

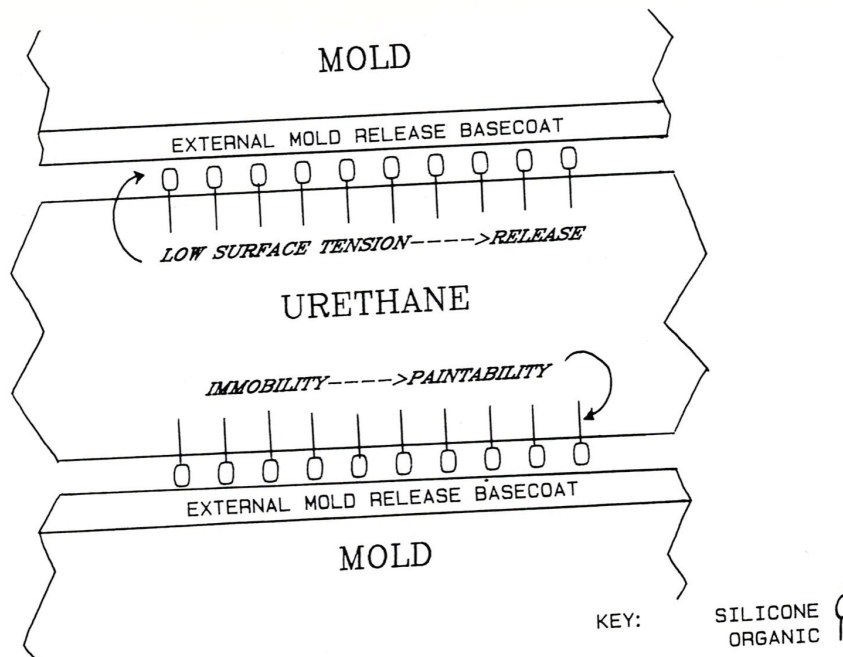


Figure 2. How silicone—organic hybrid fluids function as internal mold release agents.

CORNING® Q2-7119 as an internal mold release agent in an amine extended system. In both trials, the J-car fascia were molded using 1-2 parts of DOW CORNING® Q2-7119 Fluid per hundred parts of B-side resin in conjunction with an external mold release agent. The trials were stopped after 20 pieces were molded without a reapplication of the external release. The release was still excellent at the time the trial was terminated. The control fascia (molded without DOW CORNING® Q2-7119 Fluid) had to

rely on respraying of the mold after each cycle. As noted in the table, the silicone IMR had no detrimental effects on the overall physical properties of the resulting RIM parts.

Table 2, depicting trial results of DOW CORNING® Q2-7119 Fluid as an IMR in a glycol system, shows similar success with release and physical property retention to what was shown with the amine system. Eighteen consecutive cycles were obtained with the IMR before the trial was stopped.

In order to check the paintability of parts molded with DOW CORNING® Q2-7119 Fluid, test panels molded with and without silicone fluid were post-cured, solvent wiped with toluene, primed with PPG

Table 1. Dow Corning Q2-7119 Fluid in three stream amine extended trials.

Bayflex 110-35 System Admiral 3-Stream Machine 2.0 PHR Q2-7119		Chemtrend XMR-136 J-Car Rear Fascia	
Unfilled		5% 1/16 Inch Milled Fiberglass	
Control	With IMR	Control	With IMR
Additional T-12 (PHR)	0	0	0.50
Parts Released	1	1	20+
Physical Properties:			
Density (G/CC)	0.99	1.00	1.04
Flex Modulus (PSI)	39,000	38,900	52,400
Tensile (PSI)	3,600	3,000	2,600
6" Heat Sag (inch)	1.20	0.89	0.48
Elongation (%)	350	240	190
Two Year Florida Exposure	Excellent	Excellent	Not Run

Table 2. Dow Corning Q2-7119 Fluid in three stream glycol extended trials.

RIM 121 System Admiral 3-Stream Machine 2.0 PHR Q2-7119		Chemtrend XMR-136 Bathtub Type Mold	
Control		With IMR	
Additional T-12 (PHR)	0	0	0.2
Dabco 33 LV (PHR)	0	0	0.2
Parts Released	1	1	18
Physical Properties:			
Density (G/CC)	1.00	1.00	1.04
Flex Modulus (PSI)	101,650	101,650	110,200
Tensile (PSI)	4,300	4,300	4,200
4" Heat Sag (inch)	0.08	0.08	0.08
Elongation (%)	135	135	123

Durethane 600 Primer and then top coated with Durethane 300 blue metallic flake or white. Painted samples were exposed for two years in Florida Direct Black Box 5° South and then evaluated for appearance and adhesion. Results of these tests showed no difference between control and IMR-containing panels. Paint adhesion was excellent.

In all the trials discussed thus far, the typical RIM process was modified to necessitate the successful use of DOW CORNING® Q2-7119 Fluid. Currently, the majority of the urethane molded by the RIM process is by a two stream approach in which the isocyanate and resin sides are introduced into the mixhead as separate streams. This requires that the IMR agents be masterbatched into either or both streams. DOW CORNING® Q2-7119 Fluid is reactive towards the isocyanate side and the catalysts that are typically used in RIM systems. If placed on either side, some gellation can occur which will result in plugged filters or molded parts which paint poorly due to the exposed gels. In addition, due to the interaction of the IMR with the catalyst, cure times are lengthened and green strength is reduced. An approach which allows for the successful use of DOW CORNING® Q2-7119 Fluid is known as the three stream approach, in which three streams impingement mix at the mixhead. The third stream contains the IMR, which has been diluted with uncatalyzed polyol to aid in ratio control. Additional amounts of catalyst may be necessary in the resin components to compensate for any possible green strength reduction brought about by the reactive silicone internal mold release.

ADVANCES IN SILICONE-ORGANIC HYBRID IMR AGENTS

Although DOW CORNING® Q2-7119 Fluid is considered a three stream IMR agent for RIM, several two-stream approaches have been identified and are currently being pursued. Several highly reactive RIM urethane systems are being currently introduced to RIM molders. These systems are inherently fast reacting, and do not require tin catalyst. DOW CORNING® Q2-7119 Fluid has been shown to pro-

Table 4. Dow Corning experimental Fluids in two stream amine extended trials.

Dow Amine System Admiral 9000 3HP	Chemtrend XMR-136 '80 Mustang Front Fascia	
	Control	With IMR
IMR Concentration (% Part)	0	3.1
Parts Released	2	40+
Physical Properties:		
Density (G/CC)	0.99	1.02
Flex Modulus (PSI)	36,000	34,000
Tensile (PSI)	3,900	3,700
4" Heat Sag (inch)	0.3	0.2
Elongation (%)	310	320

vide excellent internal release capability to those systems as a *two-stream* release agent. One such system is being introduced by Texaco Chemical Company. The silicone fluid is blended into the resin side of the system and does not adversely react due to the absence of tin compounds. Multiple release with good paintability and processing has been observed with this two-stream approach. Table 3 shows the excellent release results and retention of physical properties with this Texaco system. Other unique systems which are not tin catalyzed can utilize DOW CORNING® Q2-7119 Fluid as an IMR agent.

Estimates [4] show that only 18 percent of the present RIM machines have multiple-stream capability. Although success has been demonstrated with the three-stream IMR approach, the auto industry expressed a desire to obtain a two-stream release agent. This two-stream approach would allow the RIM molder to gain release by a simple addition of the IMR agent into the A or B side. A fluid had to be found which would have the proper balance of incompatibility and reactivity in order to obtain the desired release and paintability, yet not impair the urethane cure. Dow Corning has several experimental fluids which have shown promise for release, paintability, processability and physical property retention as two stream candidates.

Table 4 shows results from an experimental trial using a Dow Corning experimental IMR agent in an amine extended system. As seen, unlike the three stream trials previously discussed, no additional catalyst needed to be used to produce good RIM parts. The internal release was added directly to the resin side. Forty releases were obtained before the trial was stopped. Release was still good at the time the trial was terminated. Also of note is the excellent retention of physical properties. In addition, initial results with new experimental silicone IMR fluids showed paint adhesion and retention to be good. Table 5 similarly illustrates results of an experimental two stream fluid in a glycol-extended RIM system. Again, excellent release and physical proper-

Table 3. Dow Corning Q2-7119 Fluid in two stream Texaco Jeffamine system.

With IMR	Control	With IMR
0.2		
0.2		
18		
Physical Properties:		
Density (G/CC)	1.00	1.00
Flex Modulus (PSI)	32,000	35,000
Tensile (PSI)	3,400	3,500
6" Heat Sag (inch)	0.60	0.40
Elongation (%)	240	230
Tear (PLI)	410	370

Table 5. Dow Corning experimental Fluids in two stream glycol extended trials.

Union Carbide Glycol System Admiral 9000 3HP	Chemtrend XMR-136 '80 Mustang Front Fascia	
	Control	With IMR
IMR Concentration (% Part)	0	4.0
Parts Released	4	25+
Physical Properties:		
Density (G/CC)	0.90	0.95
Flex Modulus (PSI)	39,000	31,500
Tensile (PSI)	3,500	3,100
4" Heat Sag (inch)	0.60	0.40
Elongation (%)	150	190

ty retention were observed. With similar levels of this experimental fluid, 25 releases have been obtained.

SUMMARY

IMR will be a wide spread reality in the very near future of the RIM industry, due primarily to the reduction in cycle time and resulting increase in productivity that are apparent through the use of internal mold release agents. Although the requirements are rigorous, versatile Dow Corning silicone/organic hybrid products can satisfy all the requirements in many systems. Dow Corning is well on the way towards successfully commercializing silicone internal mold release agents for urethane reaction injection molding. Work continues on this evolutionary development activity.

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BIOGRAPHIES

Joseph E. Plevyak

Joe Plevyak received a B.S. Degree in chemistry from the University of Delaware and joined Dow Corning in 1978. Since then, he has also received a Masters Degree in Business Administration. Joe spent four years in the Technical Service and Development Department specifically involved with silicone surfactants for polyurethane foam. In 1982, he assumed his current responsibility commercializing internal release agents for RIM urethanes. He is a member of SPI, SPE, SAE, and ACS.

Loretta A. Sobieski

Lori Sobieski received a B.S. Degree in Chemistry from Bowling Green State University and joined Dow Corning Technical Service and Development in 1976. She worked for several years in product construction markets, followed by two years in technical service for organofunctional silane chemicals. She has spent the last two years in the development of organofunctional silicone fluids for internal release agents for RIM urethanes.