

Releasants – Attachment of Coatings and use of Anti-Static Supplemental Products

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Introduction

The importance of the releasant interface in rotomolding is often overlooked and usually not given the attention it warrants. Indeed, the term “releasant” does itself no favors by not properly defining the role that the “release system” plays in the molding process. Release systems are known to influence the shape of rotomolded parts by having an effect on the plastic shrinkage during the cooling cycle. Demonstration of this phenomenon has been taken to extreme, either by design or accident, in cases where a release system has been used possessing such power that the molded part has not even formed properly before it has released itself from the mold wall. It follows reason that correct choice of release system can have a positive effect on the control of the release process and hence the quality of the finished part.

Release control achievable with the different types of mold releasant under discussion will not be explored in this paper in any depth. The focus will be placed upon how the different types make an interface with the mold wall and the durability prospects which will likely result.

The discussion on supplemental anti-static coatings is borne out of practical experiment and a theory has been proposed which fits the results observed. It examines the phenomenon of light and heavy pigmented areas within the wall of a molded product.

Throughout the following discussions, we will consider polyethylene as the most commonly used molding resin in the rotomolding process and refer to this variably as “resin” or “powder”, but note must be made that any rotomoldable material could be selected and used. The selection criteria for the release system are indeed the same, regardless of the rotomolding material being processed.

Mold Preparation

In common with any other surface coatings challenge, successful results gained from the application of releasants to any mold substrate material will be more readily achievable if a sound surface preparation regime is adopted. Whichever release system is chosen and through

whatever mold attachment method the system employs, it will function better if the substrate is correctly prepared. This principle applies whether or not the mold is new, has been taken off line for repairs, is being switched to an alternative release system or a touch-up coat of release system is about to be applied.

With time, buildup will be evident on the mold surface. The buildup will be influenced by, but not solely attributable to, the release system in use. Once the buildup reaches the point where part quality is compromised, usually through surface appearance, some sort of mold cleaning will be needed.

In rotational molding, the type of cleaning regime will be determined by a number of factors, among which are the mold material itself, mold size, accessibility of the surfaces to be cleaned, expected stubbornness of surface deposits and type of finish that is desired on the molded part. As an example, a shot-peened surface on an aluminum mold which is designed to produce a leather-look surface, will not be bead or grit-blastable because the peening will be destroyed. Likewise, a caustic liquid cleaner could seriously damage the metal surface by dissolution of the metal. In the case of highly polished steel molds, the use of abrasive pads or steel wool would make scratches and detract from the surface gloss. Some form of mild abrasive medium in conjunction with a lubricant would be a reasonable catch-all description of a cleaning regime. Generally speaking, the gentlest cleaning method, which will do the job adequately, should be chosen for the task. The basic requirement is to produce a surface, which has chemistry typical of the substrate material and has an appearance consistent with the desired part finish.

Some of the mold release attachment mechanisms described later will gain greater benefit if presented to an absolutely clean surface. Others can be applied to less-pristine surfaces with what could be considered acceptable results.

In the case of the application of permanent systems, which usually require the employment

of an outside agency, the job of mold surface preparation is usually taken care of by the contractor who carries out the job of mold tool coating.

Release System Attachment Mechanisms

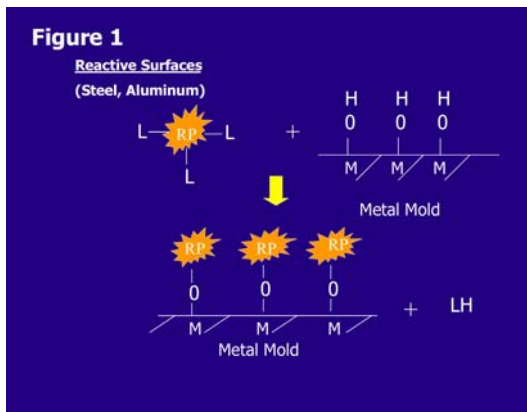
1. Reactive Systems
2. Conventional Systems
3. Permanent Systems
4. Hybrid Systems

1. Reactive Systems

These systems could be regarded as the most chemically complex.

We will consider this system first because here, the cleanliness of the mold surface achieved by the rotomolder, will have a greater influence on the success of the release system attachment process than in the other systems considered.

A cleaned metal surface will be subject to instant oxidation if allowed to sit in the open air. The substrates usually chosen for rotational molding tools -- aluminum, steel and stainless steel--oxidize at different rates, aluminum having the fastest and stainless steel the slowest rate of oxidation. Refer to Figure 1.



These substrates, which readily oxidize in air are said to possess reactive sites, typically characterized as having hydroxyl and oxide moieties protruding from the surface of the bulk metal. In other words, the cleaning process, which brought about the surface oxidation of the metal, has produced useful potential bonding sites for a reactive release system. The surface can be said to have been made “functional”.

Choose whatever method is preferred to deliver the reactive release system to the surface.

Whether sprayed, wiped or brushed, the release system will attach itself to the surface by the same mechanism. Reactive groups in the release layer consist of silicone atoms with pendant leaving groups denoted as “RP – L”, where “RP” represents the “Release Polymer”. When these groups make contact with the functionality of the mold surface, i.e., the hydroxyl and oxide moieties, a chemical reaction occurs, displacing the leaving group and forming covalent bonds between the release matrix and the mold surface. These are shown in Figure 1 as M – O – RP chemical bonds where “M” represents the metal of the mold and “O” is an oxide site. These linkages are extremely strong, the magnitude of which can be pictured if one considers that silicate rocks and minerals are built of the same chemical bonds.

The rate of formation of these bonds may be influenced by the use of a catalyst to drive the chemical reaction. Some release systems require external heat to drive the reaction forward at a rate practical for rotomolders, others use chemistry, which is activated by moisture in the air. Regardless of which kind of catalysis is used, the end result is very similar.

It is easy to understand why release systems, which employ this attachment method, are extremely durable and will allow the rotomolder to make many parts before needing to pay attention to the surface. They cannot be removed by simple solvent washing. It is possible, however, to refresh a surface coated with one of these systems and add more releasant system, renewing the release capability. Systems of this type are often referred to as “semi-permanent”.

In order to clean the metal substrate back to its original condition (when this is eventually required) it is quite normal to resort to strongly alkaline and/or abrasive cleaners. As noted in the mold preparation section, it is important to choose a cleaner that will not damage the substrate.

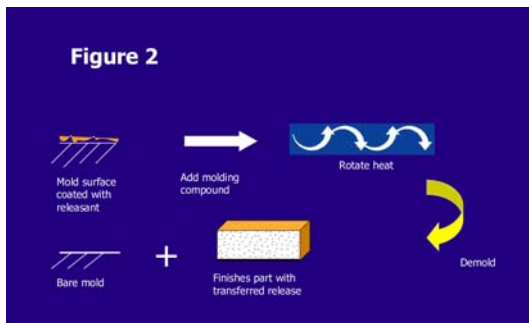
The release control or ease of release of the system is governed to a large degree by the choice and construction of the releasant polymer. The solids content of the system will also affect the release control. Discussion of these attributes is outside the scope of this paper.

2. Conventional Systems

Release systems of this type work in a completely different manner from reactive systems. Regardless of the functionality of the

substrate, it would be expected that a conventional product be added to the mold surface after each and every de-molding. One would not expect chemical bonding or attachment of any type to take place at the interface of the dried release system and the mold surface. There is no permanence either evident or implied when using this type of coating.

Typically, conventionals consist of silicone oils and wetting agents that are specifically selected for their low reactivity or functionality. Hydrocarbon oils or waxes are generally precluded because they would not be capable of withstanding the high temperature employed in the rotomolding process. Refer to Figure 2.



A conventional system would be spread over the entire surface of the mold by either wiping, brushing or spraying. Possessing no reactive sites, the system would wet and spread over the whole of the mold surface and remain essentially unchanged throughout the heat exposure cycle.

On completion of the molding cycle, it would be expected - and indeed, be a product design attribute - that the releasant detach itself from the mold wall during the cooling cycle and be removed with the molded part. Such a product design requirement is very difficult to achieve and is probably the main reason that in modern day rotomolding, conventional releasants are rarely employed.

Should a conventional be used which does not completely transfer with the molded part, the residue would be increased upon the next application of the release system. Within this residue, if there are components of the release system that degrade due to thermal or oxidative attack, they will usually discolor. Further, due to their very loose attachment to the mold tool surface, the residues will eventually sheet off and have a negative impact upon the surface appearance of the molded part.

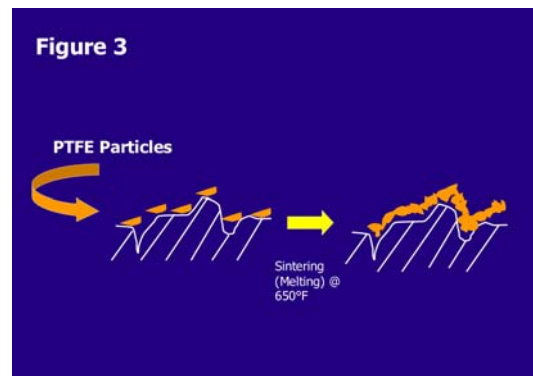
The level of dilution of the product usually governs the release control of a conventional system. Tailoring the system in order to minimize surface defects is not usually possible.

3. Permanent Systems

Back in the late 1960's and throughout the 1970's, cookware became available with the revolutionary non-stick coating based upon poly-(tetrafluoro) ethylene, commonly abbreviated to PTFE. Rotational molders have been among the many industrial practitioners that have enjoyed some of the benefits of this technology.

Unlike any of the other systems considered, permanent coatings usually require the rotomolder to employ the services of an outside contractor, both for preparation of the mold surface substrate and more especially for the coating process itself.

Figure 3 shows a schematic of the mechanism of operation of PTFE coatings.



A dispersion of PTFE, either in solvent or in a water/solvent blend is sprayed on to the surface of the mold and the carrier allowed to evaporate. Spraying is the preferred technique due to the precise film thickness control that is required and the uniformity of appearance that is desired. At this stage the layer is very loosely attached to the mold surface and as such would be useless as a release system. The coated mold is heated to approximately 650°F in what is called the sintering process, which takes the PTFE to its melt point, allowing the particles to fuse into a continuous layer.

Since PTFE is a very viscous material in the molten state, a combination of related fluoropolymers are often used which help to compensate for the limited coalescence afforded by the use of PTFE alone. The fused, continuous layer of polymers form a surface film which relies totally upon surface wetting to lock it in

place. The coating contractor has to prepare the tooling surface to accept such a film and to encourage its physical adherence.

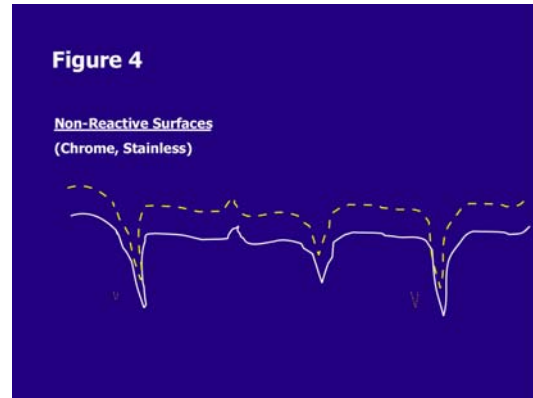
The non-functionality of a PTFE coating, which gives rise to its impressive non-stick attributes, is a double-edged sword. Coupled with the PTFE polymer's inherent softness, the reliance upon surface wetting and physical locking without the added strength of chemical bond formation makes the surface coating inherently fragile. Indeed the word "permanent" used in reference to these systems is somewhat of a misnomer: Even if the coating is treated most respectfully by the end-user, there comes a time when the whole preparation and attachment process has to be repeated. Permanency is implied, solely because no other releasant system needs to be applied to the mold tool surface until the coating is either damaged or worn out.

The actual release power generated by the coating is neither as controllable nor as selectable by the molder himself as it is in the case of alternative release systems available. Further, on-site touchup to repair a damaged area of the coating cannot be performed satisfactorily. Without the sintering treatment, patches of re-applied coating will simply be removed during the first de-molding.

4. Hybrid Systems

These systems function in a manner, which could be described as "functionally conventional". The polymeric material identified for inclusion in the liquid carrier system needs to contain some functionality as expressed in Figure 1. The amount of reactivity in a hybrid system would be typically much lower than that in a system described as fully "reactive". The presence of this lower reactivity does, however, ensure that any sites of functionality at the surface of the substrate can be used by the hybrid system, but it does not wholly rely upon this facet to bond the release system to the surface of the mold.

Hybrid systems lend themselves better to providing attachment of the release system to substrates having a much lower degree of surface functionality. An example of such a surface is stainless steel, which is much less likely to oxidize at its surface, even after a rigorous cleaning. Figure 4 shows how a hybrid system sits on the surface of the mold. It is suggested that the micro-thin layer follows the contours or the inherent surface roughness in the metal substrate.



The polymer of the release system needs to possess sufficient "cling" to allow it to remain on the mold wall throughout the molding cycle and allows the "RP" groups to perform their function of providing release control during the cooling cycle. The amount of "cling" will dictate the degree of semi-permanency achieved by the release system. The success of these so-called hybrid systems is a function of the skill employed in selection of the base polymer.

Anti-Static Supplemental Mold Coatings

The rotomolding process, by its very nature, encourages the build-up of static charge within the mold (particularly at the start of the molding cycle) due to the tumbling action of molding resin over the internal mold surfaces. This action causes "swirls" to be observed when dry-blended pigmentation is used. The swirls are either pigment-light or pigment-rich areas of the molded part and can easily be seen by backlighting a part in which the phenomenon has occurred.

In order to overcome this effect by a supplemental mold coating, it is first necessary to understand the basis of this phenomenon. At the molecular level, insulators are substances containing atoms with tightly bound outer-shell electrons (negatively-charged ions). Materials of interest to rotomolders that fall into this category are plastics and dry air. Conversely, substances containing atoms with loosely bound outer-shell electron charges allow charges to pass easily through them and are said to be conductors. Metals fall into this category.

The creation of static arises from the separation of negative and positive charges, which then build up on surfaces. Bringing two materials into contact, which are both insulators, can bring about an imbalance of charge. With some added

movement, there will be transfer of charge from one object to the other.

In a rotomolding situation, the metal mold is a good conductor; however, at the surface is a good insulator in the form of the mold release system. The molding resin is also a good insulator and therefore when the two are in contact, there is a transfer of electrons and build-up of negative charge on one surface and positive charge on the other. This phenomenon is occurring during the melt phase of the powder. It is speculated that different levels of charge will build up in different regions of the release system/molding powder interface, due to different levels of movement. If a pigment accumulates a charge, similarly charged particles will repel and unlike charges will attract. Since the pigment layer on a granule is loosely bound until the powder granule melts, the pigment will tend to move away from areas on the mold that have similar charge and be attracted to areas with opposite charge. Due to the imbalance of charge at various parts of the interface, brought about by different levels of movement, it follows that there will be an imbalance of pigment distribution because of either attraction or repulsion before the granules fuse. The granules of powder will melt in some regions of the release interface/deposited melt, carrying different levels of color intensity as a result of having either "lost" or "gained" pigment. The cumulative effect is a formation of lightly pigmented areas and heavily pigmented areas within the molding. Once all of the granules are melted and the wall of the molding is completely formed, there can be no more pigment migration.

The anti-stat layer, added over the mold release system on the mold surface, provides a medium through which the charge build-up between the molding powder and release system (the two insulators) can be dissipated.

We know from the arguments above that substances containing atoms that lose their electrons easily are good conductors. A substance has to be chosen that can be delivered to the mold wall without affecting the release properties and which will improve the conductivity of the system and help to dissipate charge.

Another factor involved in static generation is humidity and moisture content. Utilizing compounds that attract to the interface any moisture at all that remains in the powder is another way to accomplish the task of

diminishing static buildup and the resulting pigment non-uniformity.

Anti-stats are not typically durable coatings with any capability of bonding to the release layer. As such, it will be necessary to add a layer of the anti-stat product after every demolding. It would be expected that the performance of the mold release layer be unchanged.

Conclusion

Four of the primary technologies used in releasant systems for rotational molding have been described and their modes of operation detailed. By understanding the technology behind a releasant system, other key parameters such as mold preparation and cleaning, releasant touch-up, and post-molding finishing operations can be better optimized. The various chemistries available to rotational molders have been summarized with an effort to provide the information necessary to making an informed choice.

In addition, the phenomenon of static-induced pigment segregation has been investigated. As in the case of release systems, the technology and science underlying preventative measures for static dissipation can be utilized to improve part appearance and ultimately the efficiency of a rotational molding operation.