March 1992

FABRICATION NEWS

OFFICIAL PUBLICATION OF THE COMPOSITES FABRICATORS ASSOCIATION

WHAT A RELEASE!

A Technical Look At Release Agents and Non-stick Coatings

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Release Agents and Non-Stick Coatings: See How They Work

It's a question we've all asked. Why do parts stick in a mold? Why can't we predict the failure of a mold release agent?

Simple explanations for these and other problems can be presented in easy-to-understand terms. How mold release agents work, actions of their ingredients and the differences in types of release agents are presented over the next several pages.

Appearances can be deceiving

Material sciences frequently appear very technical. Learning the chemistry and physics used to understand a specific material is often perceived as both confusing and boring.

Part of the confusion stems from the fact that each science usually has its own vocabulary. Understanding the principles of a science can be like learning the language and customs of a foreign people. At first it is intimidating and difficult. But once you learn the basics you quickly begin to feel the excitement of putting these newly learned "language" skills to use as you explore a new world.

Material sciences can seem very specialized. What makes a specialist different from the general public? I was taught that a **specialist** may be described as:

1. Someone who knows how to do a particular job well; and
2. Someone who utilizes other specialists to get other jobs done well.

Everyone recognizes that a significant difference between the specialist and the general public is the vocabulary they each use to describe what they are working on. Specialists have their own language. Whether a fiberglass fabricator, a chemist, a lawyer or a doctor, each specialist uses a particular vocabulary.

BY KEITH KENT, D.M.D.

The following description of **interfacial phenomena** – what happens at the surfaces of materials – is meant to remove the mystique that surrounds mold release agents and their mechanisms of action. First, some insight into the "language" of chemistry, physics and interfacial phenomena.

Chemistry and physics

The physical and chemical "appearance" of the surface of a material is what determines how the material interacts with its surrounding environment. Surface topography (roughness) and surface chemistry control whether a material appears sticky or slippery, whether it acts as a good mold release agent or a good adhesive glue.

Again, think of chemistry and physics as a foreign language with its own vocabulary and grammar. It is easiest to learn the essentials of this and any language if you keep it simple.

The letters of the chemical alphabet are the **Elements** of the Periodic Table. These elements are the backbone of the vocabulary of chemistry. Each element has its own individual name, letter designation and number designation.

We can combine these elements, or letters, in a very specific sequence, and make different and unique chemical compounds or molecules - "nouns" in the language of chemistry. A compound is a specific combination or union of chemical elements.

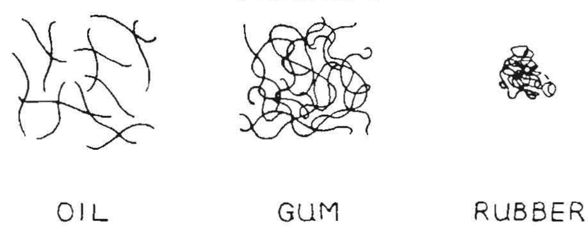
A molecule is the smallest particle of a chemical element or compound that is capable of maintaining its own chemical identity. A single atom may be a molecule and a very large compound may be a molecule. These are the same as long and short words in the language of chemistry.

These chemical "nouns," or compounds, can be combined together with a physical action "verb," such as adding heat or a catalyst and mixing. Chemical formulae are "sentences" composed of chemical compounds, "nouns," and physical actions, "or verbs." This is a rather simple but effective analysis. In chemistry, as with all languages, one can make sentences that will grow into essays and poetry.

Physics may be described as the series of rules that dictate how the letters and words of the chemical alphabet may combine and interact - like the laws of grammar that govern a language. Physics is the set of rules that determine how to assemble chemical "letters" into words and the order of the words in a chemical sentence.

As in any language, changing the order of the letters in a word will dramatically change the meaning of the word. Altering the arrangement of the chemical elements will make a different molecule or compound. The meaning of the altered word is completely different. The same is true of chemical molecules or compounds.

FIGURE 1



A polymer may be provided as an oil with short, loosely tangled polymer chains, as a gum with longer more closely linked polymer chains, and as a rubber with long tightly cross-linked polymer chains.

Polymers are composed of repeating molecules, like sequences of "letters" repeating themselves over and over again. These repeating molecules tend to form long chains that get tangled together.

"Polymer" is a popular buzz word today. However, polymers are quite common and are not new. Most chemicals beginning with "poly" are polymers, including polyolefins (waxes), polyacrylates (acrylics), polysulfides, polyvinylchlorides (PVC), polytetrafluoroethylene (PTEE or Teflon®), and polyurethanes. All of these polymers are composed of repeating molecules. **Polymerization** is the process of joining together the component molecules of the polymer. In the rubber industry, polymerization is known as "vulcanization." In the fiberglass industry, polymerization is referred to as the "cure."

Polymers are chains of repeating molecules and can be compared to tangled pieces of thread. The "threads" of the polymer are the long chains of repeating molecules. A polmer may be provided in a variety of viscosities, such as an oil (liquid), a gum (thixotropic gel) and a rubber (solid). An oil is made of short loosely-tangled pieces of "thread," a rubber is made up of long tightly-knotted tangles of "thread" (**see Figure 1**).

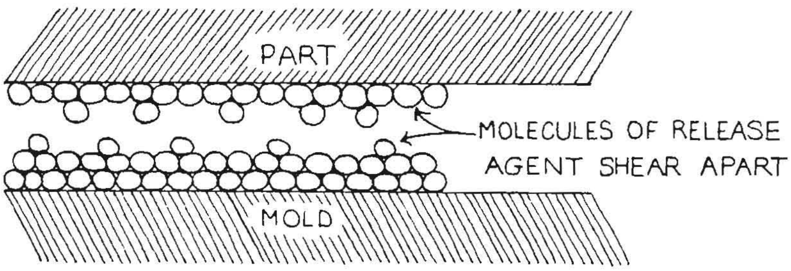
2. a "wetting agent" that makes the surface attract or wet well with the
3. "glue" that intimately adapts to the surface, proving mechanical retention.

How do standard release agents work?

Standard release agents separate a part from the material it is being molded against. Release agents tend to be from the families of relatively inert materials. Because of their lack of reactivity, these materials usually do not chemically interact with the mold or the part being molded. Their molecules also tend not to react with each other.

When separating a part from a mold, a standard release agent will undergo **inter-molecular shear,** the individual molecules of the release agent will easily tear apart from each other (**see Figure 4**). As a result, some release agent remains on the mold and some of the release agent comes off with, or transfers to, the part.

FIGURE 4



Most release agents undergo inter-molecular shear – the individual molecules of the release agent easily tear apart from each other

Surface topography of the parts plays a major role in mechanical retention. Mechanical retention may be caused by an inadequate draw path in the design of the mold.

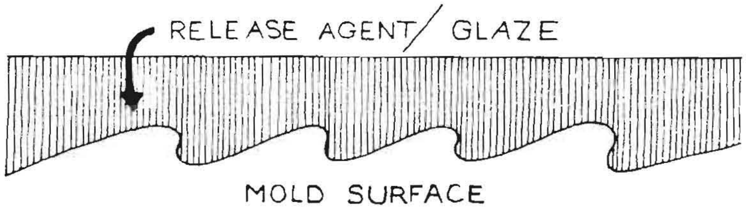
Roughness of the finish of the mold's surface(s) is also important. Composites and other materials can easily contour themselves into even microscopic defects in the surface finish of the mold and "lock" the part into the mold when the molding material hardens.

Many common release agents **smooth** the surface layer of a mold at the microscopic level (**see Figure 5**). Filling in surface defects and providing a smooth face prevents the mechanical retention that would occur on a rough mold surface.

Polishing a mold is also effective in smoothing a mold surface. *Be sure polishing agents and their residues are compatible with the materials you are molding.* Residues of polishes and other surface debris can contaminate the material being molded.

Glazes also can be applied to rough surfaces. When properly applied the glaze fills in and covers surface defects and then hardens into a new smooth finish for the surface of the mold (**see Figure 5**).

FIGURE 5



Release agents and mold glazes fill in defects in the surface of the mold and harden into a new smooth mold surface.

Ingredients of release agents

Performance of materials can easily be predicted when you understand their ingredients and the mechanisms of action of these components.

The **active ingredient** in a release agent is usually a relatively inert compound and may be a:
1. wax;
2. PTFE (Teflon®); or
3. Silicone

Due to their low reactivity, these ingredients protect the surface of the mold from chemical attack. They may smooth the surface of the mold and also may fill porosities in the mold surface. Finally, the active ingredient may also make the mold surface non-stick and/or ablative and may provide inter-molecular shear.

A **carrier** is usually incorporated to assure easy and complete wetting and total coverage of the mold surface with the release agent. After the mold's surface is thoroughly wetted with release agent, the carrier should evaporate or become a part of the release agent.

Because inert materials are non-reactive, they are difficult to "dissolve" in liquid or gaseous carriers. Usually, organic solvents and petroleum distillates are used as their carriers. Recent progress in emulsion chemistry has produced new "waterbased" release agents. However, these emulsions usually contain other additives used to make the active ingredient miscible with water. These other agents alter the chemistry of the solution and can compromise the integrity and performance of the active ingredient.

Because inert materials are non-reactive, they are difficult to "dissolve" in liquid or gaseous carriers.

Binders are also used in release agents to make the material bond to the mold surface so that it does not come off the mold as quickly, increasing the life expectancy of the release agent. Binders are also used in an attempt to keep the mold release agent from migrating to places where it is not wanted.

Fillers are used to add bulk and alter consistency. They also may include an "indicator" to show where the release agent is present on a surface.

Non-reactive materials tend to wet poorly. This can cause inadequate coverage of the mold with release agent. It also frequently causes "fish-eyes," where the material

being molded does not properly wet the mold surface. **Wetting agents** may be added to the release agent to make the surface want to wet or sheet with the material being molded, helping to prevent porosity and irregularities in the surface of the finished product.

However, when wetting agents are used the part will fit very intimately with the surface of the mold. This will cause excellent mechanical retention between the part and the mold, requiring consideration in planning the mold design. Supported areas for prying materials apart should be provided. Vents may also be used to inject air between the mold and the part to start a separation.

Inter-facial phenomena -surface chemistry and surface physics

The physical and chemical properties of a surface determine how that surface interacts with its surrounding environment. By altering the chemical "appearance" of a surface we can change the reactivity and other properties of the surface. This may be compared to applying cosmetic make-up to change one's facial appearance.

Reactive surfaces tend to interact with other materials. The more stable and chemically inert a surface, the less it interacts with the environment.

The chemical reactivity of a material is related to its **surface energy** which is measured in units of energy per units of area (such as dynes/cm2). Materials with a low surface energy tend to be non-reactive. Materials with a high surface energy have active molecules at their surfaces that are anxious to interact with other molecules.

The **contact angle measurement** is the angle a fluid makes as it contacts a surface - the "height" or angle of the bead of the fluid as it contacts the surface. The contact angle of a material to water and other fluids is an excellent indication of the reactivity of the surface of the material.

FIGURE 6

High Surface Energy
Reactive Surface
Low Contact Angle
Well-Wetted
Hydrophillic
Good Adhesion
High Surface Friction

Low Surface Energy
Non-reactive Surface
High Contact Angle
Poorly Wetted Hydrophobic
Non-stick
Low Surface Friction

Reactive surfaces interact with water and readily wet or sheet with water, having a low contact angle to water. Nonreactive surfaces do not react with water, wet poorly, and have a high contact angle.

Reactive surfaces are "hydrophilic" (water-loving) and nonreactive materials are "hydrophobic" (water-hating). A well wetted surface will have good adhesion characteristics. A poorly-wetted surface will have poor adhesion characteristics. Reactive surfaces sheet with water, non-reactive surfaces shed water. (**See Figure 6**)

Therefore, a release agent will usually provide better mold protection and easier release from the mold if it has a low surface energy. A simple field test of this phenomena is to put a small amount of water on a surface. A high water bead indicates a relatively non-reactive surface, sheeting indicates a reactive surface.

Some materials are not reactive with water but may be reactive with other fluids. This is why some release agents may have a high contact angle to water but will still wet well with another fluid, such as styrene monomer, acetone, or MEK.

Non-reactive materials also tend to have a low coefficient of friction, making them feel slippery when compared to more reactive materials. A reactive surface "grabs hold" of molecules passing over it because of its desire to react. A non-reactive surface does not attract other molecules to itself. Consider a reactive surface like a velcro ball rolling on a velcro carpet. A non-reactive surface would be similar to a highly polished ball sliding on smooth ice.

The reduced friction offered by some of the inert release agents is helpful in packing a mold or blowing a material into a mold, such as in injection molding. The less friction there is at the surface, the less force is required to inject materials against that surface.

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Porosity and density of mold materials

Fiberglass and other resins tend to be very porous and microscopically look very much like a sponge. These porosities pose several problems to the fabricator.

Abrasion of the mold's surface during even normal handling will expose and open porosities just below the surface, causing additional mechanical retention and other problems associated with rough mold surfaces.

Gases trapped in porosities under the mold's surface can expand when exposed to the heat generated during the cure of the part. This can cause surface roughness from microscopic blow holes created by the expanding gases.

For these reasons, a dense non-porous mold material performs far better than a porous (aerated) mold material. Proper mixing ratios and fabrication techniques of mold materials are critical to controlling porosity. Pressure and/or vacuum curing cycles also effect the porosity and density of the mold materials as well as of the finished product (**see Figures 7 and 7a**).

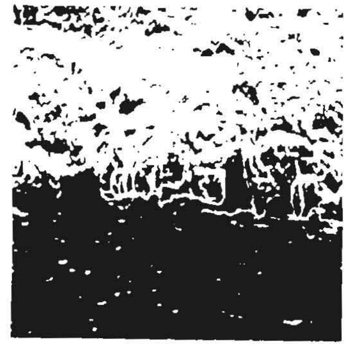
During initial curing cycles many release agents, such as waxes, are softened as a result of the heat and are forced into surface irregularities, filling in defects so that the surface appears smooth. This is one reason why used molds are less likely to stick than new molds. The more cycles including re-waxing, the better the surface is smoothed (by filling in irregularities and sealing the surface with wax) and the better the separation.

Thermoplastics and coefficients of thermal expansion

Waxes and similar release agents are thermoplastic - when they are heated during the cure cycle of the composite material the waxes soften and become plastic and/or fluid. As the mold cools, the release agent then begins to re-harden.

All materials expand and contract at different rates when exposed to changing temperatures. As the release agent, the part and the mold begin to cool they contract and the part pulls away

FIGURE 7a



Scanning electron micrograph (SEM) of material molded against a rough surface. Top half shows how rough surface of molded part; bottom half is where material was sectioned – note many porosities.

FIGURE 7

SEM of cross-section of material shown in Figure 1 when processed using a vaccum blending and cure cycle and pressure molding.

from the mold. This phenomenon is useful in separating parts that get "stuck." Dramatic changes in temperatures of the materials - heating and cooling the part and the mold - will cause all the components to expand and contract at different rates and in different amounts. This will begin the "tear" between, or the separation of, the part and the mold.

Tears tend to be self-promulgating: once you start a tear, the tear seems to want to continue to separate.

Tears tend to be self-promulgating: once you start a tear, the tear seems to want to continue to separate. This is why parts that seem stuck together will "pop" apart as soon as a tear, or true separation, is initiated. Tears can also easily be initiated by other methods of developing a shear force at the interface, including air injection and physical force.

Protection of the surfaces of the mold and of the finished part

The non-aesthetic purpose of a protective coating is to stop a surface from interacting with what comes in contact with it.

Two distinct philosophies have been followed in developing the technology of surface protection, each a compromise. One school sacrifices external performance in order to improve adherence, offering an ablative coating. The other offers an inert outer surface which, with existing technology, can be bonded to the substrate only with the penalty of high cost or limited life.

Ablative surfaces erode and are removed by wear. They require periodic replacement.

Inert protective surfaces depend upon non-reactive materials, which can only be secured to the substrate by such techniques as surface etching, heating or the application of high pressure, all of which are costly and some of which have limited effectiveness over time.

Every attempt at developing a non-stick coating has had to address the paradoxical problem that the very qualities and characteristics that make these materials desirable - their lack of reactivity - also makes them difficult to handle and apply. How does one bond a non-reactive material to a surface? Most non-stick coatings are susceptible to cracking and de-lamination, and they wear down with exposure.

Teflon®

Slightly reactive materials, such as PTFE (Teflon®), can be bonded to a surface using etching, primers, heating and pressure - all of which are costly, and some of which have limited success. These materials have poor wear-resistance and are prone to migrate, frequently causing unwanted contamination of surrounding materials.

The manufacturers of the raw materials for these inert coatings usually require application of the coating by a trained and licensed specialty applicator. Most performance claims are based upon properly bonded polymers and do not apply to over-the-counter products applied by the end-user. Consider a Teflon® frying pan. The pan is purchased with the coating already applied by a licensed applicator. If the coating is scratched or otherwise compromised, the pan is discarded rather than using the costly and difficult processes that would be required to repair the coating.

Silicones

Silicones, especially poly(dimethyl siloxane), are the most inert and chemically stable materials known to man. They are so non-reactive that it has not been possible to bond them to a surface. Silicones provide the best release of any material known. Because silicones will not react with most things they are prone to migration. They will not stick so they move about. This migration poses several practical handling problems.

When I started studying surface chemistry, a professor took me into a conference room and put a drop of silicone oil on a tabletop. He then asked me what I thought would happen to the drop of oil. I was surprised to find that by the next day the silicone had migrated and coated virtually every surface in the room.

Silicone rubber is still the most inert and chemically stable material known to man.

During World War II, silicones were developed as lubricants and insulators for submarines and high-altitude aircraft because of their ability to withstand extremes in temperature and pressure in a variety of environments. Silicone rubber is still the most inert and chemically stable material known to man.

Since silicone could not be made to chemically react or otherwise bond with a surface, sheets of silicone would be made and these sheets would be stapled or otherwise physically attached to the surface. The sheets of silicone had poor tear strength and wearability and this process is usually not considered practical or cost-effective. Recent efforts attempt to "bond" silicones to another base layer of coating material such as an epoxy. These materials also have poor wear strength, are extremely technique sensitive and require a multi-step (S+) application.

Blending non-sticks with other materials

In the past, researchers have attempted to incorporate inert materials like silicone or Teflon® into other coatings as a matrix or binder, hoping that levels of the stable material would aggregate along the surface of the cured coating. Results were disappointing.

Adding silicone or Teflon® to a paint usually turns the material into a "non-paint." The material will not bond to the substrate and quickly peels away. The inert ingredients are also prone to migration. Since they do not react with and stick to a surface, they easily move from place to place. As these materials migrate, they contaminate any surface they may contact. Repairs or re-painting of a surface contaminated with an inert material is nearly impossible. However, marketing the "benefits" of minute amounts of non-stick polymers incorporated into other materials continues to be popular despite the many inherent problems of these blends.

Mixing with other materials such as binders and fillers also diminishes the inert material's beneficial characteristics.

Mixing with other materials such as binders and fillers also diminishes the inert material's beneficial characteristics. If any benefits are gained, the performance of the coating is only enhanced for a short period of time. The binders also introduce other problems. As an example, they are usually rigid and have a different coefficient of thermal expansion than the surface of the substrate. With fluctuations in temperature, the coating expands and contracts at a different rate than the underlying material, causing the coating to crack and de-laminate.

Research and future direction

Research efforts are focused towards developing new mold release agents that are:

1. Environmentally safe;
2. Long-lasting;
3. Easy-to-use; and
4. Utilize tethered polymers.

Repair materials are rarely finished as smoothly as the original mold surface. The repair materials also tend to be very porous. Proper polishing and sealing of the repair material is critical.

Application of mold release agents in solvent carriers may enhance penetration of the release agent into porosities in the repair material.

Self-bonding polymers offer the easiest repair since they are bound to the surface of the mold and do not migrate into the resin like other release agents.

Other applications of these principles

The principles of surface chemistry and physics discussed here may be applied to many other areas besides mold release agents. A material that will protect a mold will also protect the finished product. Non-reactive release agents usually reduce drag and sliding friction. Simple contact angle measurements (putting a drop of water on a surface) can be used to determine surface reactivity, wettability and adhesive character. ■