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Title: Adhesion Problems: Who is Responsible?
Author: Tim Cowell- Technical Director- Die Casting and Metal Working Fluids
Company: Hill & Griffith Co. Inc

Introduction

Die Casters and Casting Finishers have long been at odds over adhesion problems. When a Finisher experiences coating or adhesive failures, he /she typically points to the die release agent used in the die casting process. The Die caster, who manufactures other castings using the same die lubricant that presents no problems for other finishers, believes that this particular finisher's process is at fault. Unfortunately, a lot of time and resources are expended trying to solve this problem.

To shine some light on this mystery, this article will focus on the following:

- What are the Forces that create Adhesion?
- What are the Conditions that prevent Adhesion?
- How do Die Casting Release Agents Impact Adhesion?
- What are the Keys to assuring proper Adhesion?

The scope of this paper will be limited specifically to metal – polymer adhesion such as e-coating, powder coating and adhesives.

The Forces that create Adhesion

Despite the large amount of literature written about the concept of adhesion, nobody still knows the specific details of how these various forces collectively work together to create these phenomena. The American Society for Testing Methods (ASTM) in section D 907 defines adhesion as:

> ***"The state in which two surfaces are held together by interfacial forces which may consist of valence forces or interlocking action or both".***

Although there are several theories concerning the forces that make up adhesion, within the metal finishing industry, the consensus is there are two primary mechanisms that creating the metal – polymer adhesive bond; chemical ***bonds*** and ***mechanical interlocking***.

Chemical Bonds

There are two types of chemical bonds that contribute to adhesion, ***Van der Waals*** and ***Ionic***. A detailed discussion of the nuclear interactions that take place between the different atoms and molecules is beyond the scope of this paper, therefore a basic definition for each type of bond will be given and a description on how the chemical bonds contribute to adhesion of the polymer to the metal surface.

Ionic Bonds

An ***Ionic Bond*** is a chemical bond formed by the electron attraction between positive and negative ions.

Ionic bonds are created when an electron from the valence shell of one atom is transferred to the valence shell of another atom. The atom that lost an electron becomes a positive ion and the atom that gains the electron becomes a negative ion. An example of this type of bond is NaCl or table salt, where the Na+ (Sodium) ion carries a ***positive*** charge and the Cl- (Chloride) ion carries a
negative charge.

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Van der Waals Bonds

Van der Waals bonds are forces that result from the interaction of the positive and negative charges between neighboring atoms or molecules. These bonds exhibit themselves in very long chain molecules that make up polymers that are part of our everyday life, such as rubber and plastics.

The electrons (negative charges) of an atom or molecule ***A*** will repel the electrons of an atom or molecule B, but will attract the positive charged nuclei of atom or molecule ***B***. The electrons of atom or molecule ***B*** will repel the electrons of atom or molecule ***A*** but will attract the positive charged nuclei of atom or molecule ***A***.

Based on this interaction of attraction and repulsion, equilibrium between the two atoms or molecules is established between 4 and 10 angstroms. Any distance smaller than 4 angstroms is met with resistance and ***repelled***. Any distance greater than 10 angstroms is met with resistance and ***attracted***.

Although the strength of the ***Van der Waals*** bonds are individually fairly weak, collectively, they represent a significant force in the make-up of the adhesion bond.

While it is not known which type of chemical bonding is predominate, it is known that a combination of both ***Van der Waals*** and ***Ionic*** bonding takes place between specific components of the polymer (coating) and the reactive hydroxyl groups / metallic ions that form the skin on metallic castings, particularly aluminum.

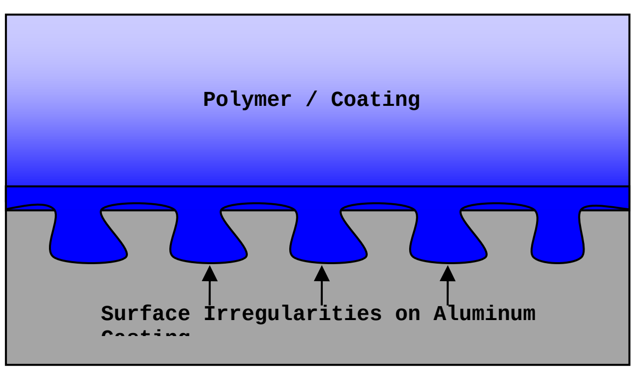
Mechanical Interlocking

Although chemical bonds are a significant contributor to the adhesion bond, the primary force behind adhesion is Mechanical ***Interlocking***.

Unlike chemical bonds, ***Mechanical Interlocking*** is an easy mechanism to understand. In Mechanical Interlocking, the substrate's (aluminum surface) roughness provides a mechanical interlocking or keying system that allows the polymer and the substrate to bind together. See diagram below.

The polymer is allowed to flow into the crevices and solidify creating the physical bond. It has been demonstrated several times that a light mechanical abrasive treatment on a substrate often increases the adhesion bond strength.

Figure 1.1



MECHANICAL INTERLOCKING

Within this mechanism, the strength of the adhesion bond is directly proportional to the polymer coating and the condition of the metallic substrate.

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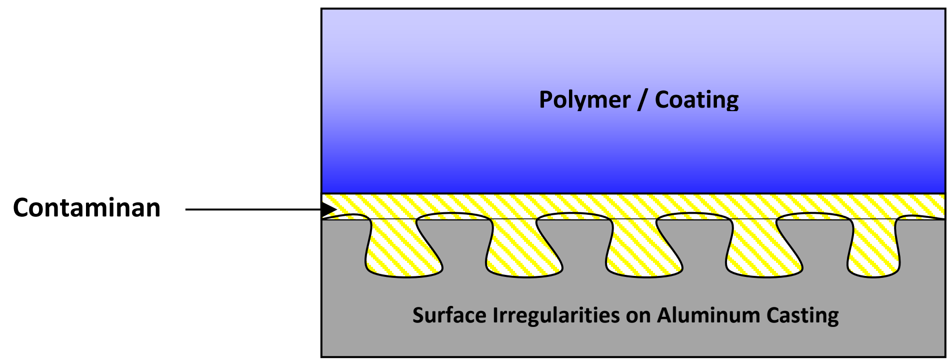
The Conditions that prevent Adhesion

The answer to this question is fairly simple. It is the antithesis of what creates adhesion.

Any material, organic or inorganic, or process that prevents the organic polymer or coating from having intimate interfacial contact with the metallic substrate will inhibit or prevent the adhesive bond from forming. See figure 1.2.

Figure 1.2



How do Die Release Agents affect Adhesion?

In order to understand how the release agents, affect adhesion, one must have a general understanding of the release agent's role in die casting and the thermodynamics of the process.

Thermodynamics of the Die Casting Process

Die-Casting is a thermodynamic process of injecting molten metal into a steel die under intense force. The alloy being cast is held under pressure until it solidifies into a specific shape, referred to as a casting.

This thermodynamic process exists in a state of equilibrium. What is meant by equilibrium is that the heat or BTU's (Basic Thermal Units) introduced into the process are removed from the process.

HEAT IN = HEAT OUT

Although the amount of BTUs introduced into the process are fairly constant (determined by the temperature of the metal, the size of the part, etc...), the philosophy of the die casting manager determines the amount of BTUs taken out (cycle time, heat transfer fluids, spray time) and ultimately whether the process runs at higher temperatures or lower temperatures.

Role of the Die Release Agent

Once a die caster has determined the cycle time and the number of BTUs that can be removed from the die through heat transfer, then caster often utilizes the release agent spray time to accommodate the removal of the remaining BTUs necessary to maintain the optimum equilibrium for the casting process.

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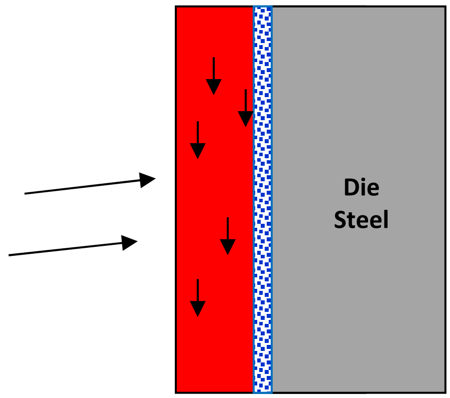
The die release agent is a vital part of this process. It is a complex mixture of organic components that are sprayed onto the die to prevent the metal of the casting from integrating or sticking to the metal surface of the die (Figure 1.3).

Figure 1.3

DIE RELEASE AGENT (BLUE)

MOLTEN METAL (RED)



When the molten metal hits the die release agent, it begins to undergo thermal decomposition. The heat breaks down the material into elemental carbon (black material) and other various decomposition byproducts. This carbon creates the insulating barrier that allows the casting to release and prevents the metal from interacting with the carbon steel on the die.

It is crucial that the die release agent's manufacturer understands how the die casting manager's philosophy of die-casting before recommending a product. If the die caster runs his/her die at higher temperatures, then the product that is recommended incorporates the appropriate chemistry to accommodate the high heat and the optimum ratio is determined.

How the Die Release Agent Impact Adhesion

Under theoretically ideal conditions, there would be just enough die release agent present on the die surface to totally decompose leaving just the thin carbon film. However, in reality, due to large variable fluctuations in the process that impacts the thermodynamics of the process (start up, down time, variable spray patterns, hot spots on the die, etc.…), this will never happen. Therefore, when the die release agent's ratio is determined for a particular casting process, its basis is to accommodate the hottest part of the die to allow for proper release of the casting and protection of the die. Unfortunately, this ratio allows for small amounts of partially decomposed release agent to remain on the cooler parts of the die and casting surface. Often this organic residue is not visible to the naked eye, however it this residue, if not removed, that will create adhesion problems.

The Keys to assuring proper Adhesion

It has been often said that cleanliness is next to Godliness. This is particularly true when it comes to preparing the metallic substrate for coating. Following are the keys to preparing the substrate for proper adhesion of the coating.

1. ***Know the contaminants that are being removed.***

   Too many times a casting finisher does not involve their pretreatment chemical supplier with the die release agent's manufacturer to discuss what types of contaminants will be present on the castings. So, when the finisher runs several lots of castings through the coating system and experiences a significant amount of failures, the finisher immediately points the finger at the die caster for using a release agent that cannot be cleaned.

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The typical contaminants associated with the use of die release agents are:

- Oils (Petroleum or Synthetic)
- Emulsifiers
- Waxes
- Siloxane (Paintable) Polymers

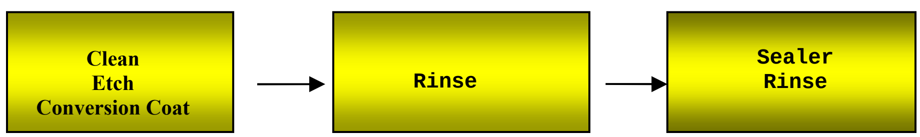
2. *Design or Adjust the Pretreatment System to remove these types of Contaminants*

There are six keys to cleaning the metal substrate. They are

System Design

There are many different pretreatment system designs ranging from 2 stages to more than 10 stages. However, the most common with the metal – polymer coating industry are the 3 to 5 stage systems.

3 Stage Pretreatment Systems



5 Stage Pretreatment Systems

It is reasonable that the more cleaning and rinsing stages that a casting goes through the cleaner the part. Therefore, it is understandable why many of the finishers who have utilized 3-4 stage designs in the past for economic reasons, have been upgrading to systems that utilize a 5 stage or more for the added cleanliness that it yields.

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Chemistry

Cleaner

The most popular and most used aqueous cleaners used today are the high alkaline cleaners (pH >10.0). They are very effective against stubborn soils. However, most of the alloys used in the casting process (aluminum, zinc and magnesium) are attacked by these high alkaline cleaners.

Consequently, either mild alkaline cleaners containing inhibitors or neutral cleaners are used. The problem with neutral cleaners is that they are too mild. As was mentioned before some of these die lubricant residues are very difficult to remove. The mild cleaners are also more difficult to monitor than alkaline based materials.

The recommended chemistry for cleaning metallic casting surfaces is a strong surfactant-based product that is mildly alkaline with a pH between 8.5 and 9.5 and contains corrosion inhibiters.

Treatment

Once a casting has gone through a cleaner and been rinsed it is subjected to an acid bath of some type to remove any oxides on the surfaces that may have formed in storage or transportation. Often an Iron Phosphate Treatment is used to etch the surface of the alloys as well put on a conversion coating in preparation of the coating. While this is effective when preparing steel parts to be coated; with aluminum, the normal acids do not etch the part and the reaction between the phosphate and aluminum never takes place. Therefore, the majority of the pretreatment processes have incorporated an ammonium bifluoride, which creates a weak solution of hydrofluoric acid. This type of acid will readily etch the aluminum surface creating fresh sites for the **Mechanical Interlocking mechanism** of adhesion to take place.

Water

The chemistry of the water can impact the overall coating process, by leaving hard water deposits on the casting surface. Ideally the Pretreatment Tanks need to be monitored for excessive hard water salts build up.

Temperature

Die lubricant components are designed to withstand the heat of the die casting process. Therefore, it should not be a surprise that heat must be generated in the removal process of its decomposition products.

Heat enhances the cleaning by:

- Synergistically increasing the chemical activity of the cleaner

  It is a known that the chemical reactivity of the cleaner is directly proportional to increases in temperature. This increase in activity allows the surfactants to get under and lift off the contaminants as well as etch the surface in preparation for the coating.

  Please note: *It is important to make sure the temperature and chemical concentration are controlled to avoid excessive etching (smutting) especially with aluminum alloys. This smutting can and will cause adhesion problems as well.*

- Liquefying stubborn contaminants such as waxes or high molecular esters that exist in a solid state when not emulsified.

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Low to medium melt point waxes and siloxane (paintable) polymers can sometimes be removed with a low alkaline cleaner running at temperatures of about 130 - 150º F , however high molecular polyethylene (synthetic) waxes do not begin to melt until much higher temperatures (160 – 180 º F). These types of waxes require that the casting substrate be heated sufficiently to the point that the wax begins to melt and allows the cleaner's surfactants to get under the contaminant and lift it to the surface where it can be removed by the washer spray or agitation.

The heat should be held between 160 – 170˚ F. If the temperature is much lower than this, some of the residues will not soften and be removed.

Spray Pressure (Mechanical Energy)
Too many times, people forget that cleaning is not only a chemical process but also a physical one. Chemical cleaning requires the surfactants to be able to interact with the soils. However due the stubbornness of many soils (high temperature waxes), mechanical energy is required to do the actual removal of the soil from the substrate. Spraying is a more effective means of removal than immersion or dunking.

The higher the pressure, the more efficient the cleaning process. Recommended pressure is between 15 – 20 psi but is often determined by the geometry and size of the part.

Time
You can have all the proper components in the Pretreatment System, but if the process does not allow enough contact time between the part and the treatments, the parts will not be properly cleaned and prepared for coating.

Proper Maintenance
Proper maintenance of the process and equipment must be done to consistently provide a clean part to the coating system.

This includes chemical checks, water pressure checks, nozzle checks to make sure that they are not plugged up and spraying the right locations and temperature checks.

3. Post Treatments

Recently, many finishers have incorporated post treatment operations after the pretreatment to assist with the adhesion process.

- Baking ovens, where the castings are raised to a temperature of 400 F for periods ranging from 15 minutes to 60 minutes. This is to eliminate any remaining organic contaminants that might create out gassing (raised deformities) or prevent proper adhesion.

- Plasma Treatments

Within this process a plasma field is formed when flammable gas and air are combined and combusted to form an intense blue flame. Brief exposure to the energized particles within the flame affects the distribution and density of electrons

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on the substrate's surface and polarizes surface molecules through oxidation. This method also deposits other functional chemical groups that further promote adhesion.

Flame plasma treaters generate more heat than other treating processes, but materials treated through this method tend to have a longer shelf-life. These plasma systems are different from air plasma systems because flame plasma occurs when flammable gas and surrounding air are combusted into an intense blue flame. Objects' surfaces are polarized from the flame plasma affecting the distribution of the surface's electrons in an oxidation form. *(www.plasmatreating.com)*

Summary

It is the author's hope that the information shared in this paper will enlighten both the die caster and the finisher regarding specific steps to take in troubleshooting and resolving future adhesion problems. Always remember that the die casting process and the coating process are at opposite ends of the spectrum. The die caster utilizes a specific die release agent to resist removal by molten metal, allow for release of the casting and protect the die, thereby optimizing his / her casting process. While the finisher wants a residue or contaminant that is easily removed from the casting and allows for optimum adhesion of the coating. Because of this, it is imperative that all parties involved with the casting and coating process; the die caster, the finisher, the die release agent manufacturer and the pretreatment chemical supplier get together to discuss how to address the contaminants on the casting before there are adhesion problems.