Chemistry: The Core of Cleaning

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There are thousands of specialty metal cleaners available to industry. Understanding the chemistry behind cleaning compounds is essential to matching the best practice product with your process situation, and then maximizing its performance capabilities. An overview of specialty cleaners, their basic chemistry components, strengths, weaknesses, and relative cost comparisons will be presented in the context of frequently asked practical metal cleaning questions.

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Working on projects initiated by your superior is a normal, everyday event. It is a typical morning, the coffee is brewing, the inbox is full of new things to do, but what is this, it's a note from your boss, "see me ASAP." Oh no! Is this it, is this the end, have the higher-ups decided to "reorganize" and in doing so decided to eliminate my position; or has all my hard work finally paid off?

Prepared on two fronts you march into your boss's office. On the one front you are prepared to do your best Michael Keaton impression of "take this job and shove it" and on the other you are prepared to graciously accept the promotion that you have longed for. Twenty minutes later out of the office you walk, over to the mezzanine balcony where you take a deep breath and grin; proud ownership of all metal cleaning operations is yours. Its a tough job, now what are you going to do?

As a Cleaning Operations Manager, you have complete control over all cleaning operations. You are responsible for the cleanliness of all production parts. You evaluate all new products for their material capability, health, safety, environmental impact, cost, optimization, and most important of all, their effectiveness. Wow, all of this responsibility, and then it dawns on you, what do I know about industrial cleaners?

There are thousands of specialty metal cleaners available to industry and a plethora of chemical companies. Understanding the chemistry behind cleaning compounds is essential to matching the best practice product with your process situation. Gaining an understanding of specialty cleaners, their basic chemistry components, strengths, weaknesses, and relative cost comparisons will be essential to your success and maximizing performance.

The first question is why do we clean? Cleaning is often performed as an in-process procedure to remove contaminants prior to assembly. Removing metalworking fluids, rust prevents, and shop soils from the work make handling in-process work easier and more efficient from an operator standpoint. In addition, in-process cleaning helps improve safety.

Cleaning is also a necessary step of chemical treatment prior to painting and plating. Operations that require chemical reactions or electro-adhesive processes require a contaminant-free surface to be effective. For example, a phosphate conversion coating reaction requires complete contact of the surface with the conversion coating solution. Soils act as a barrier that prevents the reaction from occurring. The resulting insufficient coating ultimately results in corrosion and adhesion failure. In regards to plating or electrochemical deposition processes, soils act as an insulator. This prevents even current distribution leading to uneven coating thickness or absent coatings.

Cleaning prior to Brazing, Soldering, and Welding is necessary to prevent the generation of toxic fumes and the formation of colored tenacious heat scales.

Cleaning is often performed as a last step in a particular production process. As a last step, manufactured goods are often cleaned for aesthetic purposes. We all expect that when we buy our new white refrigerator it won't be covered with someone's greasy/dirty fingerprints.

All of this sounds reasonable, but additionally there are almost always customer specifications and cleanliness requirements. Equipment needs to be scrubbed for maintenance purposes, tow motors need to be cleaned, tools and hand equipment need to be maintained and the list goes on and on.

To fully understand cleaning we need to understand soils and contaminants. To describe a contaminant as a lubricant, grease, oil or simply as dirt is to grossly understate the reality of the cleaning situation. Each of the aforementioned contaminant types contains complex combinations of significantly varying molecular ingredients. Soils and contaminants in general can be broken down into two different categories: organic and inorganic. Organic soils are those that are based upon hydrocarbon chains. As the name indicates, these compounds consist exclusively of the elements carbon and hydrogen. Organics are derived principally from coal tar, petroleum, and plant sources. Common organic soils include fats, decayed matter, oils, mold and fingerprints. Conversely, inorganic soils are those materials that are not based on hydrocarbons. Typical examples of inorganic contaminants are: laser scale, rust, grinding particulate, different oxides and hard water scales. Soil can be inorganic, organic or some combination of both. Examples of these are: rust inhibitors, coolants, lubricants, mold release compounds, and metalworking fluids.

What makes certain soils so difficult to remove? To answer this question is to understand the molecular and atomic forces that hold substances together. Many types of forces exist that hold molecules together to ultimately form substances that we classify with names, for instance, "soil." The strongest of these forces is interatomic valences sharing or covalent bonds. All of us have seen the ball and stick model representation of atoms, bonds, and molecules. While these models are a good tool to visualize and conceptually grasp atomic bonding, it does not do justice to the scientific reality. Zooming in on an atom close enough to get a visual understanding of the interactions that result in molecules is an impossible task.

Analytical testing has provided enormous amounts of information about the characteristics and interactions of atoms and molecules. Famous scientists such as Schrodinger took this data and used mathematics and statistical thermodynamics to develop models that on a quantitative level replicate very closely the reality of the data.

Application of these models to other molecules shows a very close correlation. These models, observations, and data were all used to develop scientific laws that have not been refuted. The models developed, from a visual standpoint, contain a central nucleus or core composed of positively charged protons and neutral neutrons. Surrounding this core are electrons flying about in defined areas known as orbitals. Orbitals have specific shapes and can be visualized as clouds surrounding the central core of the atom.

Each element or atom has a different numbers of protons, sometimes neutrons, and/or electrons. Many factors contribute to how strongly the electrons in these orbitals are held to the nucleus. The resulting electron retaining strength is often called electronegativity. Under certain conditions different elements will orient themselves so that their electron clouds overlap, resulting in a sharing of electrons. The resulting condition is called covalent bonds involving two atoms, each donating one electron to form a pair held between the two atoms. Such bonds are generally formed by atoms with little difference in electronegativity...i.e., carbon, hydrogen and oxygen. This sharing results in the combination of two atoms existing as a whole with a lower energy than the sum of the individual atoms. The lower the overall resulting energy the stronger the bond.

Now that we understand how atoms are combined to make molecules we look at how molecules are held together to make realizable materials. Forces of major interest are those associated with hydrogen bonding. A hydrogen bond is an attractive force or bridge that occurs between the slightly positive (electron deficient) end of one molecule and the negative (electron abundant) end of another molecule. This type of bonding is about one tenth the strength of the covalent bond but has a major effect on properties such as melting and boiling points. This interaction is responsible for holding molecules together. The most notable substance that displays this phenomenon is water.

The final type of force that will be discussed is called "van der Waals' forces. These are weak attractive forces acting between molecules. They are weaker forces than hydrogen bonds. Electrons will be unevenly dispersed around an atom or molecule at any given time, meaning the molecule will have a slight positive charge on one end and a negative charge at the other. This temporary state may cause attraction between two molecules, pulling them together. When properly oriented, these molecules will attract each other. These forces often called electrostatic attractive forces are responsible for holding dust and other particulate to substrate surfaces.

Many other forces exist but these three will give you an understanding of what cleaners are doing from a molecular/atomic viewpoint. In order to dissolve a soil a cleaner must be able to diffuse through the soil and breakdown or disrupt the natural binding forces within the soil. Now we are getting to the meat of the discussion or the chemistry of cleaning.

Recalling your high school chemistry class, you will remember something about "like dissolving like." Having similar "like" chemistries enables mixing to occur due to attractive forces between the chemical cleaner and the soil. Also, the diffusion coefficients involved in mass transfer are at their greatest (maximizing mixing efficiency) when similar materials are introduced. Disrupting the molecular attractive forces that bind the soil together is just one way that a cleaner is effective. The other is on an atomic level where some cleaners act to change the molecular composition of a soil, thus disrupting atomic and molecular binding forces.

When a cleaner is effective at permeating or atomically changing composition of the soil it disrupts the matrix of adhesive forces holding it together. With a weakened matrix the soil or contaminants can be swept away, leaving a "clean" surface.

So now you see why we clean, what we are cleaning, and how chemicals work to remove soils, but now what? How do you know which product to choose you ask? The first step in choosing or evaluating a new cleaning chemical is to understand what is in the cleaner and what your soil is composed of. For example, if you can identify your soil as non-polar, then your chances of successfully dissolving the soil using a non-polar cleaner are increased greatly. Remember "like dissolves like." When you are comfortable with a type of chemistry that will be effective at cleaning a particular soil, you must evaluate specific products that are non-detrimental to your substrate. A chemistry that cleans a soil but attacks the substrate, in most cases, is deemed unacceptable.

Two major classifications of cleaners are solvents and aqueous cleaners. Solvents by definition are considered to be substances that are capable of dissolving another substance resulting in a uniformly dispersed mixture at the molecular level. Aqueous cleaners consist of many different chemical species that make water a more effective cleaner.

Solvents are sub-classified as being either polar or non-polar. The term polar is applied to some solvents because of the uneven electron sharing-density distribution across the atoms of the molecule. Molecules such as oxygen and nitrogen have a strong electronegative meaning that electrons or negatively charged particles spend more time around them than the other atoms in the molecule. This unequal electron spread can be thought of as creating a molecule with different poles. In the simplest case a two-pole molecule exists with one end being more negative than the other. The most common polar solvent, often referred to as the "universal solvent," is water. Allowed enough contact time water will dissolve almost everything. The rock of the southwest over hundreds of thousands of years has been dissolved by water forming the Grand Canyon. Other examples, of polar solvents include methyl-ethyl ketone and methylene chloride.

Conversely, non-polar solvents essentially have a non-distorted electron-sharing characteristic. The majority of hydrocarbon solvents (organic) are non-polar. As a generalized statement, Aromatic Hydrocarbons, or those molecules that contain at least one ring structure in their atomic geometry, are stronger solvents than aliphatic or alcohol substituent containing solvents. Common non-polar solvents will often contain ethers, esters and amines.

Solvents are used extensively in the paint coating field, in industrial cleaners, pharmaceuticals, and in the printing industry. Everyone knows that water and oil don't mix, therefore heavy-duty industrial cleaners cleaning tenacious oils and greases often use solvents composed of petroleum distillates. Again, "like dissolves like."

What should you consider when evaluating solvent cleaners? While highly effective, flammability, toxicity, contribution to air pollution, fire hazards, characteristic irritant properties, and high costs have led to the decline of solvent use as industrial cleaners. Solvents should not be discharged to a sewer or the environment. Disposal is usually arranged through a licensed disposal company or treated by special Waste Disposal Sheet. Additionally, the majority of solvents are insoluble in water. Without water as a carrier the solvent is used to break up the force matrix in the soil and must also act as a carrier to remove the soil from the substrate. In general, most solvents are used straight and on a use cost basis are very costly.

With the gradual decrease in solvent cleaning chemicals, for the reasons listed above, aqueous cleaning has emerged as the primary substitute in metal pretreatment systems. While solvent products can consist of blends of solvents to make them function on broader soil types, aqueous cleaners are far more complex in their composition. What about using just water as a cleaner? You recall that water is considered the universal solvent and given enough time will dissolve virtually any material. The key here is "given enough time." Remembering that water is a polar substance that has extensive hydrogen bonding and knowing that most oils, greases, rust prevents, and metalworking fluids encountered in industry are non-polar in nature, you can see how water alone would be ineffective at cleaning these soils. The water and the soils don't mix so water doesn't have the opportunity to do its job at dissolving the soils. Therefore water is combined with other materials that enable the water and soils to mix and in some cases to react to chemically change the makeup of the soil itself.

Aqueous cleaning is accomplished by various mechanisms, including saponification, emulsification or dispersion. Saponification of fat based compounds by alkaline chemicals allows them to be dissolved into a cleaning solution. Emulsification by cleaning chemicals allows insoluble liquids to mix. Dispersion is the process of lowering the surface tension between the cleaning chemical, soils, and the metal surface. This dispersion leads to the subsequent removal of the soil from the metal.

Industrial aqueous cleaners include many different chemical species that can be organic and/or inorganic in classification and can be powder or liquid in form. Generally, aqueous cleaners contain three generic groups of chemicals with varying functions. These groups are referred to as builders, surfactants, and additives. Additionally, aqueous cleaners can be considered acidic, alkaline, or neutral in nature. Acid cleaners have a pH of less than 7, alkaline cleaners usually contain alkali metal salts and have pHs greater than 7, and in general neutral cleaners are composed of surfactants and their blends with pHs arround 7.

Builders are the basic building blocks or foundations of an aqueous cleaner. Typically builders are inorganic alkali metal salts. The strongest of the alkaline builders are hydroxides such as sodium hydroxide and potassium hydroxide because they fully dissociate (every molecule has full capability of providing reactivity). Remembering from our previous discussion, a cleaner either changes a soil's chemical composition or breaks interactive forces that hold the molecules together. Builders function to react with the soils, changing their chemical composition and thus dissolving their structure. Hydroxides are used extensively to convert fatty acids that are found in natural oils to soap. This soap is then relatively easy to sweep away with the water carrier. However, this reaction, depending on the soil, can often lead to foam generation which may be unacceptable. These strong alkaline builders will react and change the composition of a metal surface as well. Without cleaning components built into the product, these builders may not be suitable for use on soft metals such as aluminum and galvanized. Remember, what is the soil, what will clean the soil, and will the cleaner affect the metal substrate.

Silicates are often used as a component in industrial aqueous cleaners. Silicates have the ability to block previously loosened soils from redepositing on the substrate once they have been removed. This is part of a chemical phenomenon known as emulsification. They are used to provide multi-metal safety by inhibiting the attack of a metal surface by the alkaline salts such as the hydroxides. Another reason silicates are used is to provide a source of reserve alkalinity. Unlike the strong hydroxide builder, the silicate does not completely dissociate right away. It sits in an equilibrium state between partial and complete dissociation. As the alkalinity that the partial dissociation provides is consumed, then the equilibrium is shifted and the molecule completely dissociates providing a second wave of alkalinity. Twice the bang for your buck!

Phosphates are found in some aqueous cleaners as a source of reserve alkalinity. They are relatively inexpensive materials. When combined with highly alkaline builders or surfactants, phosphates are very effective at dissolving mineral oil based soils. Additionally, the posssess water conditioning characteristics.

Less effective than phosphates are carbonates. Carbonates provide reserve alkalinity and are among the least expensive builders. Carbonates also act as water softeners, precipitating hard water salts that may interfere with other cleaner components.

Surfactants are another builder that serve many purposes in an aqueous cleaner. Different classifications of surfactants exist, each with different characteristic properties. The four main types of surfactants are anionic, cationic, non-ionic, and amphoteric. In general, surfactants are organic molecules that are characterized by being bi-functional. Bi-functional meaning that the molecule has two different distinct ends with specific functions. One end of the molecule has a chemical composition such that it has a strong affinity to water and is known as a hydrophilic end. The other end of the molecule is water hating and has an affinity for oils and other non-polar liquids. This part of the molecule is known as the hydrophobic end.

Surfactants known as surface-active agents perform several tasks in the cleaning operation. The first task is to lower the surface tension between water and soil, allowing the two to mix. Oil and water do mix! The second task of a surfactant is to have its hydrophobic end attach to the soil. When water is flushed along the surface of the soil the end of the surfactant that is water loving holds on to the water. Ultimately the soil is lifted from the surface by the action of the water and the bond with the surfactant molecule. Third, the surfactant will encapsulate the soil, also known as micelle formation, preventing it from redepositing on the freshly cleaned surface. Some surfactants also cause the soils to coagulate and split from the cleaning solution where they can be mechanically removed from the cleaning solution.

Cleaning additives are where all other cleaner components fall. These additives have very specific functions depending on the range of the cleaner. Some examples of additives are materials that provide metal safety or EDTA that is added to sequester metals in solution and as a conditioner to tie up hard water salts.

Alkaline and neutral surfactant cleaners are generally used exclusively on organic soils. Tough soils may require highly alkaline cleaners with surfactants added as a builder to aid in cleaning. Lighter organic soils may require strictly a neutral surfactant cleaner. However, inorganic soils usually require an acid cleaner with or without surfactants added.

An acid can be thought of as a molecular substance that breaks up, in water solution, into hydronium ions and a corresponding anion. The hydronium ion is considered a proton donator or electron deficient species and the corresponding anion is an electron rich species. Some acids donate only one hydronium ion and others have the capability of donating multiple ions. The lower the pH of an acid solution the more hydronium ions it contains. Most acids are inorganic in nature, i.e., Phosphoric, Nitric, Hydrochloric, etc. In general, inorganic acids are stronger acids than organic acids but industrial cleaners can contain both. Examples of organic acids include Citric, Glycolic, Oxyalic, etc.

Inorganic soils require the proton donating capabilities that an acid will provide. For example, weld scales, heat scales, hard water scales and all inorganic soils are relatively inert (non-reactive) in comparison to organic soils. A hydronium ion in acidic solution is highly reactive and will steal electrons from other molecules in order to become stable. The scales provide the reaction sites and ultimately the electrons that the hydronium ions want. The molecular structure of the scale is broken down to the point where it is dissolved and flushed away by a water carrier. Because the acids are essentially dissolving the scales and the metal surface, metal safety is definitely a concern with acid cleaners.

Because aqueous cleaners are additives that assist water in cleaning they are generally far less expensive than solvent based cleaners. Depending on soil type and load, the required concentration of an aqueous cleaner can vary significantly but in general it is less than 10% of the total cleaning solution.

Most cleaners will require some type of waste treatment process depending on local disposal regulations. Some surfactants can be sent directly to drain while most alkaline and acidic cleaners at a minimum require neutralization. Everyone is responsible for understanding their local and statewide disposal laws.

Chemistry is the fundamental science behind cleaning technology. In understanding the basic chemistry of cleaners you learn about all the other aspects that go into making the right cleaning product choice. Becoming the resident cleaning expert will not only solidify your position it will ultimately ensure your success as Cleaning Operations Manager.