COSMOS – GUIDE 2

Guide for Coating Industry Executives and Technicians:
The Essentials of Chemistry and Physics in Paints & Coatings

Paints and coatings are a practical expression of chemistry and physics. Everything that happens in the design, manufacturing, application and drying of paint is physics and chemistry in action. Understanding the chemistry of paints definitely provides a professional edge over peers and can even open doors to new job opportunities with contractors. The goal of this Guide is to provide painters with conceptual tools to understand the basics of how paints work internally. Let's start with one of the most well-known chemical reactions: the oxidation of steel.

CHEMICAL REACTION INTUITION

Did you know that industrial steel, as we know it—strong and tough—had to undergo a process that goes against nature to become what it is? Steel is not thermodynamically comfortable unless it is corroded. In natural conditions (without human intervention), steel prefers to be oxidized and become an oxide; that's why in nature we cannot find intact industrial steel unless it has been cared for. But… what does thermodynamically comfortable mean?

It's easier to understand the concept of 'thermodynamically comfortable' if we imagine that all molecules are like tiny magnets. What would happen if we place 5 magnets in a space where they are relatively close? Their opposite poles will attract and like poles will repel. In summary, they will move from one position to another. Now, what would happen if we introduce our hand between these magnets? They can no longer join as they did before because now there is an element (our hand) weakening the magnetic attraction forces. When our hand is not present and we place the magnets back in that space, all these magnets generate magnetic attraction and repulsion forces that are perceived by other magnets. The magnets receiving these forces feel excited and want to move towards or against the emitting magnets. This is what is known as thermodynamic excitation and represents an unstable situation. Why is it considered an unstable situation?

It is considered an unstable situation because the magnets will not stay where they are; they will move due to themagnetic attraction forces. This is what happens with steel. Industrial steel, as we perceive it, is a matrix of billions of tiny magnets organized in rows and columns held together by electrical forces. Chemically, these forces are called “metallic bonds,” and the orderly arrangement is called “crystalline.” However, all chemical bonds are electrical, so our analogy with magnets works perfectly.

There is an important detail worth considering. In the example described above with the 5 magnets, what would happen if after the 5 magnets have moved and the system is in equilibrium, we were to place a new magnet, but it happens to be 100 times weaker than the original 5? The answer is that this last magnet will also emit magnetic forces, but they won’t be strong enough to move the other 5 magnets, which are already joined and stable.

Something similar to what we have just described happens with steel atoms, but in reverse. These atoms, like tiny magnets, are stable and bonded, forming the hard and solid matrix of steel, but a much stronger magnet, abundant in our atmosphere—the oxygen molecule—appears. Suddenly, the stable arrangement of steel starts to overexcite and gain energy, meaning that these magnets are no longer comfortable. Now they want to react with the oxygen. The oxygen molecule has the power to steal the valence electrons from the iron atoms in the steel and break their metallic bonds. The result is oxidation. Of course, the actual phenomenon has many more technical details and is more complex, but this gives us a good summary.

As mentioned, it is evident that steel is quite vulnerable to corrosion, as it is thermodynamically unstable due to one of the most common molecules on our planet: oxygen. It’s ironic that steel, being so hard and resistant, finds its integrity exposed and vulnerable to this tiny molecule. On the other hand, steel is one of the pillars of modern industry and construction. Protecting it from deterioration and fracture is crucial for societal safety. However, it is not only exposed to corrosion but also to mechanical wear and chemical deterioration. Given all these dangers and the supreme importance of ensuring steel's integrity during its use, mastering the art of its protection is vital.

Now, in the market, there are various types of paints, which can be confusing if you are not familiar with chemistry. First, we will explain what paint is, and then we will cover the different types and their properties.

PAINT ELEMENTS

Paint is composed of 4 elements: solvent, binder, fillers/pigments, and additives, of which only the binder, fillers, pigments and some additives remain in the solid paint layer; the solvent and some additives evaporate during the drying phase.

SOLVENT

Broadly speaking, the function of the solvent is to allow all the molecules in the mixture to move. Without the solvent, each molecule would remain bonded to its pairs and could not react with other molecules. That’s why once everything has reacted and the paint is solid, the solvent is no longer needed and must be expelled through evaporation.

BINDER

The binder is like the structure of a building. Once it solidifies through polymerization during the curing phase, it allows the fillers and pigments to be trapped in its matrix. The binder is one of the major factors affecting the mechanical, chemical, thermal, optical, and electrical properties of paints. Think about it for a moment: if the structure of a house is made of wood or the arrangement between beams is poorly designed, it will not withstand an earthquake very well. The same happens with the binder in a paint system. On the other hand, a compact and dense structure will allow fewer chemicals to penetrate the paint. It acts as a particle filter, reducing the likelihood of a chemical reaction. But the most important consideration regarding the chemical resistance that a cured binder can offer is the strength of its bonds and the obstacles it creates around vulnerable areas that prevent the passage of chemical agents. The stronger a bond, the more energy is needed to break it, and the more steric hindrance or bulk around the bonds, the harder it is to break them.

FILLERS / PIGMENTS

Fillers and pigments are components added to paint to increase its mechanical strength, provide color and give it anticorrosive properties. As the name suggests pigments are responsible for color but they also function as elements that make the paint harder and more resistant; the primary function of fillers is to enhance durability.

Imagine that pigments and fillers are like spheres, and the binder is like a steel cage with interconnected supports and beams. Now imagine placing those spheres inside the cage where they become trapped but are in contact and tension with the cage’s beams. What we're doing here is increasing the distribution of stresses when tension is applied to the binder. This means that now each part of the cage will endure less stress because the load is transferred to the hard and resistant filler particles. The fillers now help to resist these stresses.

Not all fillers and pigments need to be spherical; they can also be flat, layered, or have various shapes. Each structural form will interact differently with the binder. Another significant benefit, particularly of lamellar fillers, is that they increase the paint’s impermeability, meaning they make it more difficult for chemical agents to penetrate the matrix. This happens because, as flat particles, they cover gaps in the same way a coaster covers the top of a glass when placed on it.

ADDITIVES

Finally, additives are substances or particles introduced into the paint to provide specific properties that the binder and fillers alone cannot offer. These can include increased elasticity, reduced viscosity, better adhesion to metal during drying, smoother bonding between binder molecules, among others.

Depending on the specific type of binder, we will have different paints with various properties. The most common in the market are Latex and Enamel (Gloss) paints. Then there are more specialized ones like epoxy and polyurethane paints. Each paint has its function and was invented for a particular purpose. It is important to be aware of the limitations and strengths of each type to make the right decision when purchasing. Below, we outline the main characteristics of each.

LATEX PAINTS AND ENAMEL (GLOSS) PAINTS

PROPERTIES

Latex paints were designed to provide the following properties: fast drying, easy application, good washability and good coverage. Enamel (gloss) paints, while also having these properties, are primarily valued for their shiny finish, as their name indicates. However, while both types of paint offer a certain degree of durability and resistance, they cannot be compared to the chemical and mechanical resistance provided by specialized protective paints such as epoxy and polyurethane. We will delve further into the chemistry of paints to demonstrate this.

RESINS AND CURING

Latex and Enamel (gloss) paints are formulated with either alkyd or acrylic resins. During the drying and solvent evaporation phase, alkyd resins cure by reacting with oxygen in the environment, while acrylic resins do not cure but have strongly attracted chains. So, what is curing? Curing is the chemical process by which strong chemical bonds are created between functional groups of two pre-polymeric chains. Curing gives paints hardness and resistance. It is important to note that all specialized and strong paints cure; it is a fundamental stage.

We mentioned that acrylic paints do not cure, but alkyd paints do. So, if alkyd paints cure, why isn't their resistance comparable to specialized paints? The issue is that curing alone is not a sufficient guarantee of hardness and resistance. It can provide these attributes but not necessarily. Think of curing like an arm holding something about to fall. If only one arm is holding it and the object's weight is heavy, that arm may not be sufficient; more arms may be needed. The same applies to chemical curing. The number of cross-linked bonds between pre-polymeric chains is what makes a structure more resistant, much like many arms supporting something would provide more stability. This is the case with specialized paints like epoxy and polyurethane, which have a high level of cross-linking and, therefore, greater hardness and resistance.

EPOXY PAINTS: 2-COMPONENT SYSTEMS

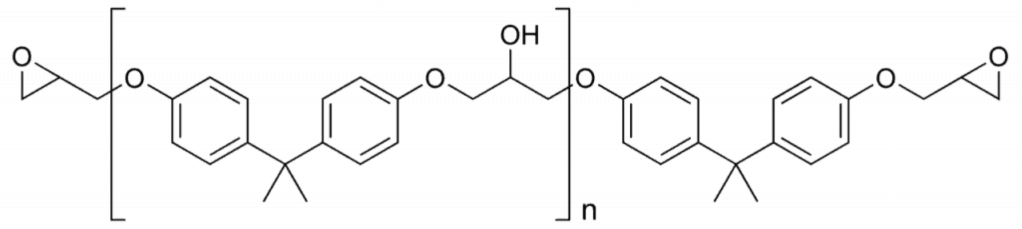
Epoxy paints are two-component systems: the epoxy pre-polymer itself and the hardener. So what is a pre-polymer? To understand this, we first need to explain polymerization, which is the type of reaction that cures thermosetting resins. Polymerization involves molecules joining together with strong bonds to form a single giant molecule. That's why it's called a polymer: poly (many) and mer (units). So how does this relate to pre-polymers? If the polymer is the giant macromolecule of cured epoxy resin, the pre-polymer is precisely the epoxy resin units that will join when they polymerize upon meeting the requirements of their bonding. These pre-polymers are sold by major chemical product manufacturers and can be obtained in either solid or liquid form. Since we need them to be applicable in the 2-component system, if they are purchased in solid form they must first be dissolved in an appropriate solvent.

We should also emphasize the oxirane or epoxy group. The oxirane group consists of two oxygen atoms bonded to two carbon atoms (C_2H_4O) at the ends of the molecule. Each epoxy pre-polymer has two oxirane groups. These are the groups that will react with the hardener from part B during curing. They are highly reactive groups, and we need to ensure they react only with the hardener.

PART A OF EPOXY PAINTS

There are many types of epoxy pre-polymers, but the most commonly used is DGEBA or Diglycidyl Ether of Bisphenol A, as shown in the image. It consists of two aromatic rings forming the skeleton of the molecule, connected to two epoxy or glycidyl groups through an ether linkage. That's where its name comes from.

So, part A is comprised of the epoxy resin pre-polymers: the units that will later join. These pre-polymers look like this:

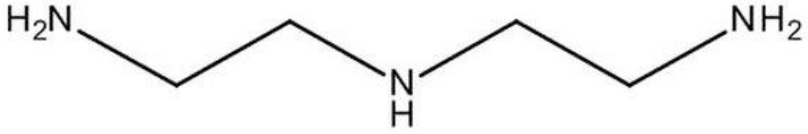


PART B OF EPOXY PAINTS

Part B is the hardener. The hardener is responsible for bonding the DGEBA through the oxirane groups. As you can see, there are two oxirane groups per pre-polymer, so each molecule can bond with two hardeners. There are epoxy pre-polymers with more oxirane groups per molecule (e.g., two on each side), but while this would provide greater cross-linking and hardness, it would also make the paint very rigid and brittle, which is not ideal where more flexibility is needed.

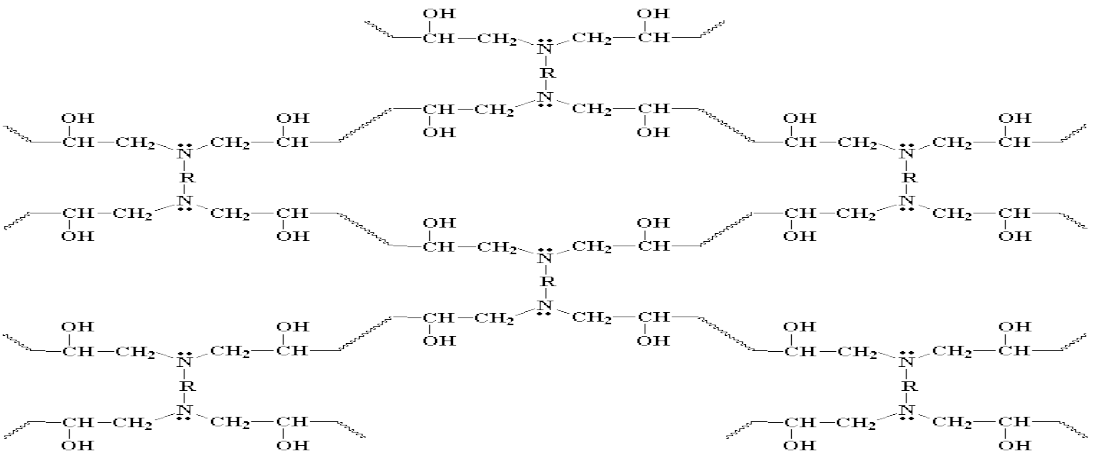
In Part B, there are many types of hardeners, but the most commonly used industrially are polyamides and polyamines. In practice, adducts of these molecules are used, where many amines or amides are joined to form a single large molecule. However, for educational purposes, we will discuss these molecules individually.

One of the most commonly used polyamines is triethylenetetramine (TETA). As shown in the figure below, this molecule has three amine groups in its structure: at the two ends and in the center. An amine group is a nitrogen atom bonded to carbons and hydrogens. These groups will connect to the oxirane groups of the epoxy pre-polymer. We can see that each TETA molecule has three nitrogens or three active groups, so theoretically, each molecule can connect with three epoxy pre-polymers. It is important to know that although it can theoretically connect with three, the central nitrogen has side atoms that create steric hindrance around it, making it more difficult for the oxirane group to access. This makes the central nitrogen less reactive than the primary nitrogens located on the sides. As a result, this central nitrogen often remains unreacted, and the molecule may end up cross-linking with only two pre-polymers.



THE REACTION BETWEEN PART A AND PART B

So, how does this reaction occur? In the oxirane group, the carbon bonded to the oxygen is electron-deficient because oxygen is a strong electron attractor and pulls the shared electrons towards itself. This makes the carbon partially positively charged. On the other hand, the nitrogen in the hardener has two free, non-bonded electrons. These electrons carry a partial negative charge. Opposite charges attract, so when the hardener molecule approaches with the precise orientation to that oxirane carbon, the reaction happens. The oxirane ring opens, the carbon bonds to the nitrogen, and the oxygen of the oxirane group pulls a hydrogen from the nitrogen. Once this occurs, the hardener is bonded to the epoxy pre-polymer via one nitrogen; but remember, each nitrogen has two sides, and each molecule has three nitrogens. This means that each hardener can potentially connect with 2x3=6 epoxy pre-polymers! This is a significant number. This is why cured epoxy resin is extremely hard and resistant. A very compact matrix forms, consisting of structures or bonds that are difficult to break, as the amine and oxirane ring bonds formed are resistant. The result of the curing process can be seen in the image below. The chains (H-N-H) are the amine hardeners, and the wavy chains ending in (-CH3) are the chains of the epoxy pre-polymer.



This image is a cross-sectional or two-dimensional approximation, but this structure is actually three-dimensional, and we can see that per volumetric unit, there is a lot of mass or chains. Each of these chains is linked to others via the amines. If we compare it to a construction, we might deduce that this cured resin is a well-articulated structure that maximizes stability against any external stress. It is important to know that the greater the density and structural coordination, the more stresses are distributed, and each section will be subjected to less stress, which is essential to prevent the formation of cracks in the structure. Cured epoxy resin possesses this quality and thus has great durability.

HIGH CHEMICAL RESISTANCE

We have discussed the mechanical resistance provided by cross-link density, but another important characteristic is its high chemical resistance, primarily due to three factors: steric hindrance, physical barriers and thermodynamically stable functional groups. Steric hindrance is the blocking action performed by functional groups next to others to prevent contaminants from coming into contact with reactive groups. In the image of the cured structure, for example, the CH3 group on the chain obstructs any particle from coming into contact with the two free electrons of the amine nitrogen. On the other hand, the physical barrier refers to the structure's impermeability. As mentioned earlier, the formed structure is of high molecular density and compactness, making the pores or channels from the outside to the interior of the paint very narrow or even closed, obstructing the entry of potential contaminants that could react with the paint. When we talk about contaminants with the potential to react with the paint, we are referring to extreme cases where there is a very high or low pH or high temperatures. The groups within the structure are quite stable. It takes a lot of energy for them to react with external agents. So, even if the physical barrier and steric hindrance are bypassed, significant temperature or specific pH conditions are needed to chemically degrade the binder.

EPOXY RESIN IS ANTICORROSIVE

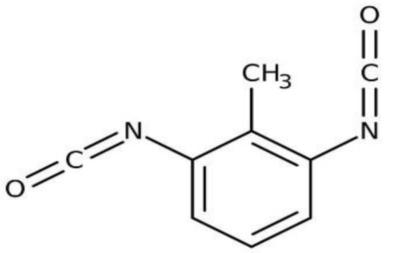
Epoxy resin is also quite anticorrosive, although this is more due to the pigments than the binder itself. The binder simply provides a matrix for the pigments to anchor. These pigments offer what is known as cathodic protection through anodic sacrifice to the metal substrate. Essentially, this means that the pigments sacrifice themselves by donating their electrons so that the substrate does not oxidize. This is because all metals have an oxidation potential that represents the stability of different metallic atoms.

There are atoms that have excess electrons and feel very unstable with them, while others wouldn't mind gaining an extra electron. We know that metals in contact form a circuit through which electrons of the same metals can flow (this is how current moves). So, if we have a metal at one end of the circuit that prefers not to have electrons and another at the other end that wouldn't mind accepting them, the electrons transfer between them. When a metal atom loses electrons, it generates a formal positive charge on that atom. In an aqueous medium, this pigment atom (now a positively charged cation) will be dissolved by the water, which has a negative region. The sacrificed atom detaches from the solid pigment it was in and becomes dissolved in the water.

Gradually, more pigment atoms dissolve until the pigment completely disappears. Meanwhile, the substrate remains intact and solid. As we can imagine, cathodic protection is possible as long as sacrificial anode pigments exist. Once all are corroded, the substrate metal becomes vulnerable. Therefore, it is important for a paint to contain a considerable amount of sacrificial anode pigments. One of the most common is titanium dioxide.

POLYURETHANE PAINTS

The curing logic for polyurethane paints is very similar to that of epoxy paints; analogously, the only difference is the building blocks and the cement. The building blocks of epoxy paint were DGEBA and polyamines, respectively; in polyurethane, these are polyisocyanates and polyols. The main difference between epoxy and polyurethane paints is that the former are specialized for interiors because, without additives, they suffer from poor ultraviolet light resistance. This is due to the aromatic rings in epoxy. These rings have electrons in "pi" orbitals that absorb and resonate with the frequency of ultraviolet light, making it possible for UV light to photodegrade them. The most commonly used polyurethane paints also have aromaticity in their structure, as in TDI (toluene diisocyanate), but the difference is that it has only one ring, while each epoxy prepolymer has two rings. This makes polyurethane paint better for finishes or for use in exteriors. We can see the TDI structure in the image below.



The polyurethane system is also composed of part A and part B. Part A consists of the prepolymers and part B is the hardener. As indicated by the name, we do not use isocyanates alone but typically use isocyanate adducts in part A to achieve a polyisocyanate molecule. This makes it less toxic by creating less volatile molecules and provides more active groups for forming more crosslinks with polyols, resulting in a harder and more resistant final structure.

Regarding the reaction mechanism, similar to epoxy, polyols react with isocyanates through nucleophilic addition to form crosslinks. It is important to know that a polyisocyanate molecule normally has between two and three active isocyanate groups ready to react with the polyols in the hardener. On the other hand, the most commonly used polyol type is hydroxylated acrylic resins. The term "hydroxylated" indicates it has polyol groups (O-H); acrylic resin is a compound that can be polymerized, with each unit having a hydroxyl group. If we polymerize three acrylic resin molecules, we will have three active hydroxyl groups ready to react with the isocyanates. Thus, if that's the case, we would get 3 isocyanate groups x 3 hydroxyl groups = 9 crosslinks! A significant number. These crosslinks are what give polyurethane paints such good mechanical and chemical resistance.

IMPORTANCE OF PIGMENTS IN MECHANICAL RESISTANCE

While we have discussed the good mechanical properties of hardness and resistance provided by the binder when dry, it is important to note that a significant part of the mechanical resistance is provided by the pigments and fillers themselves, after all, they are metals. Metals are highly resistant, and binders act as the glue holding them together, so they must be hard because the maximum hardness of a system is determined by its weakest component. However, it is the fillers that provide maximum resistance. This is partly because they are highly dense: their atoms are packed very tightly. Therefore, it is crucial that pigments are well distributed in the paint and that their percentage is optimal.

SURFACE PRETREATMENT

We may have the most durable and resistant paint, but if it does not adhere well to the substrate, it will peel off. The first step for good adhesion is to ensure contact between the paint and the substrate. This contact will not be optimal if there are contaminants like grease, salts, or oxides on the substrate. If so, the paint cannot interact with the substrate. Surface pretreatment is one of the most important processes in applying industrial protective paint. There is a saying: “A low-quality paint on a well-treated substrate will be more effective than a high-quality paint on a poorly treated substrate.” Removing these contaminants should be done with detergents for grease and acids for difficult-to-remove oxides; of course, everything should be rinsed with water to dissolve and remove the resulting products.

ADHESION

Last but not least we now look at one of the most fundamental factors for achieving good protection: Adhesion.

Once interaction between the paint and the substrate is possible, the goal is for the paint to spread over the metal and maximize the surface area to which it adheres. You may have observed how water droplets remain as spheres on some surfaces; that’s exactly what we want to avoid. This happens because water molecules are more strongly attracted to each other than to the metal. This is called surface tension. Water has a relatively high surface tension. On the other hand, metal attracts water weakly. As a result, water will have a better contact zone with the metal and will adhere only at that limited point. This issue is addressed starting at the point of paint formulation. Low surface tension solvents, such as organic solvents, are sought, and if they cannot be used, wetting agents are used. These are low molecular weight molecules that reduce the surface tension of the solvent.

Finally, one of the most effective methods to improve adhesion is abrasive blasting, sanding, or sandblasting the metal surface. This is done to create a rough surface on the metal. A rough surface creates a larger area for the polymer to penetrate and adhere. This increased surface area creates more adhesion points with the polymer and improves the paint’s durability.