

# MATERIALS FOR IRON CONSERVATION

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# IRON AND ITS ALLOYS

Like many other metals, iron can form alloys with metallic or not metallic elements. The most common alloy element for iron is carbon. However, modern iron alloys contain a lot of different elements like chromium, nickel, copper, etc.

The principal iron base alloys are:

- Wrought Iron;
- Steel;
- Cast Iron.

# WROUGHT IRON

Wrought iron is nearly pure iron with less than 1% carbon and about 2,5% slag. This was the only type of iron produced until 18<sup>th</sup> century.

Metal extraction, in antiquity, occurred in carbon coke furnaces. These kind of furnaces cannot extract liquid iron from its ores, but a spongy, iron-rich material (*bloom*). Hammering and heat treatments were needed to obtain the well known silvery metal.

# STEEL

Steel is an iron alloy with 2% carbon or less. Industrial production of steel started in 19<sup>th</sup> century, with the invention of Bessemer process, although the extraction method from cast iron was discovered in 16<sup>th</sup> century.

Modern steel is a complex alloy with elements like chromium, manganese, nickel, vanadium, etc. Inox steel, for example, has an high concentration of chromium, that lead to the passivation of metal surface. A particular example of modern steels is COR-TEN (CORrosion resistance, TENsile strength steels).

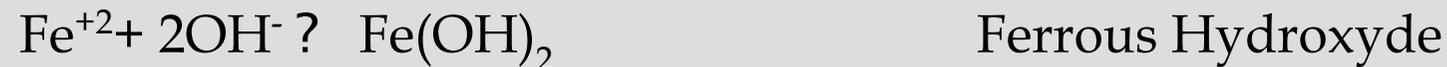
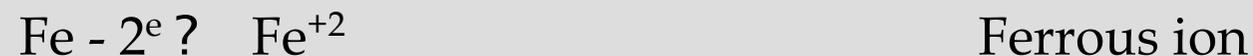
# CAST IRON

Cast iron contains carbon from 2% to 6%. In ancient times it was considered a “waste material” and it was used principally for cannons or anchors. In modern times, it was used for extraction of steel.

Actually, cast iron can be found in objects like manhole covers, grindstones, and other materials which shall resist to abrasion.

# IRON DEGRADATION

The main degradation of iron and its alloys is the formation of corrosion products, called rust. Rust is a mixture of oxides, principally hydroxides of iron(III). Typical reactions in rust formation:



Ferric hydroxides react with iron core remained.

# MORFOLOGY OF CORROSION

Corrosion products on various iron alloys are always the same, but morfology can be very different. Some examples:

- Pitting: it is due principally to chloride and/or presence of moisture. This form of localized corrosion can lead to perforation.
- Crevice: in heavily pitted or stressed materials (i.e. bended), the metal surface can crack.
- Galvanic corrosion: when two different metals are in direct contact, in presence of an electrolyte (i.e. salt water), corrosion occur at the interface due to formation of a galvanic cell. It can lead to total destruction of “less noble” metal.

# ENVIROMENT AND CORROSION

	Acetate	Carbonate	Chloride	Hydroxyde	Nitrate	Phosphate	Sulphate	Sulphide
Marine	-	I	S	I	S	-	S/SS	I
Burial	-	I	S	I	S	I	S/SS	I
Internal	S	I	-	I	-	-	S/SS	-
External	S	I	S	I	S	-	S/SS	-

S = Soluble, I = Insoluble, SS = Scarcely Soluble

Enviroment has a great influence on iron artefacts degradation, which can be found in good or bad conditions. Generally:



This scheme gives only an idea of corrosion degree. Many factors can intervene, slowing down or speeding up corrosion rate.

# PRELIMINARY STEPS

Rust layers are not chemically stable, but sometimes can be a better choice to leave them on iron surface, because gasses and water permeation is slowed down by the presence of oxides and encrustations. Primary conservation steps are:

- Fast drying: natural drying can lead to corrosion for the presence of oxygen in the air. Corrosion rate slows down on dry materials. Acetone can be used for its high evaporation rate.
- Inhibitive solutions: iron can achieve passivity in controlled pH solutions. If necessary, iron can be stored in solution of sodium hydroxide (pH 9-10).
- Controlled storage atmospheres: nitrogen atmospheres can help iron conservation, subtracting oxygen and moisture from iron storage environment.

# RESTORATION OF IRON

As above mentioned, corrosion morphology changes, but restoration treatments are always the same. Iron restoration could be summarised in three main steps:

- Cleaning: desalination, removal of dust, ancient protective layer and corrosion products.
- Stabilization: inhibition baths, conversion of oxide layers, consolidation, structural reinforcements.
- Final protection: coatings or varnishes (protective layers).

If necessary/possible, an artefact can be consolidate, reconstruct with fillers, stored in controlled atmospheres, etc.

# DESALINATION

With a conductivity meter is possible to establish the presence of soluble salts in washing solutions. In most cases, soluble salts are chlorides or nitrates; their presence speeds up corrosion rate more than 10 times.

Conductivity parameters are expressed in Siemens/cm or ppm. The higher is the value, the higher is soluble salts concentration. Before measuring solutions, it's better to make a "*blank*" measure on pure demineralized water for a reference value. Normally demineralized water is about 5 mS/cm.

# CLEANING

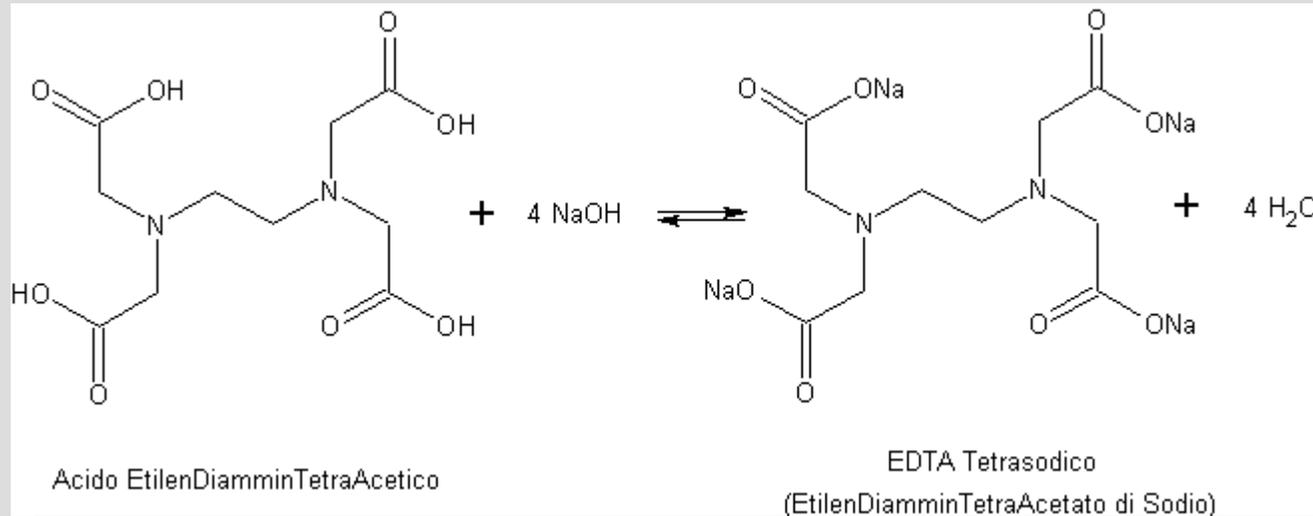
- Mechanical: with micro-sandblast, scalpels, brushes, etc. These instruments are useful for thick encrustation and artefacts without ornaments (chasing, gilding, inclusion of other metal or materials).
- Chemical: with complex forming agents (tetrasodic EDTA, ammonium citrate, etc). In case of ornamental objects, chemical cleaning can preserve little particulars.
- Electrochemical: not feasible on heavily corroded/frail objects, because hydrogen stripping can lead to lost of some parts.

# EDTA

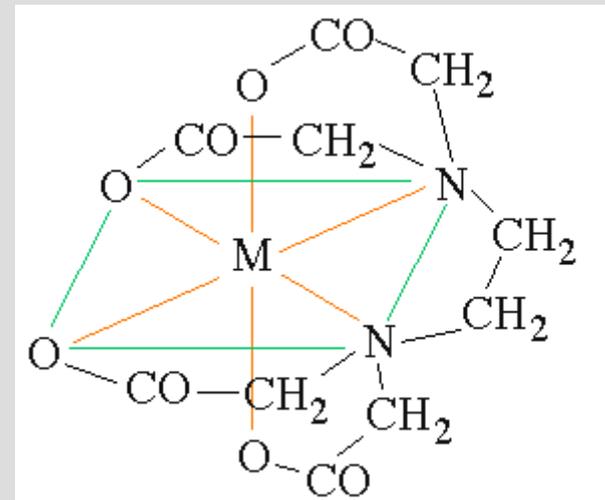
Tetrasodic EDTA is one of the most common complexing agents used in restoration. Also bisodic EDTA is commonly used because remove rust faster. Although, tetrasodic EDTA is average 11 pH, bisodic EDTA is average 5 pH; acids on iron objects can begin corrosion.

Tetrasodic EDTA complexes faster calcium than iron, so if there are red iron oxydes on a calcareous stone it is better to use bisodic EDTA, which subtracts iron particles first and than reacts with calcium.

# TETRASODIC EDTA STRUCTURE



Like crab's chelas, EDTA can catch a metallic ion. It is called "chelate effect". Oxygen (O) and nitrogen (N) atoms in EDTA structure strongly attract positive ions. Complex forming agents frequently contain O and/or N (amins, ammonia, citric acid, etc).



# INHIBITION

An inhibitor is a compound or a layer which slow down/block metal corrosion, forming a barrier on the surface or reacting with oxydating agents.

Inhibition on iron can be achieved with compound such sodium hydroxyde or sulphide. However, it's not possible to include these inhibitors in some polymeric protective layers (i.e. acrylic), so they only can slow down corrosion rate for a brief time lapse.

# RUST STABILIZATION

To stabilize rust layers, which cannot be removed, it can be used a rust converter. Commonly, commercial rust converters contain tannic acid and phosphoric acid, but also some polymers, i.e. acrylic ones, which form a film layer on the surface and reduce converter's penetration.

The choice of the proper converter depends on artefacts' storage environment. Phosphatizing agents are needed for artefacts in external environments, for museum objects it's possible to use tannic acid solutions instead.

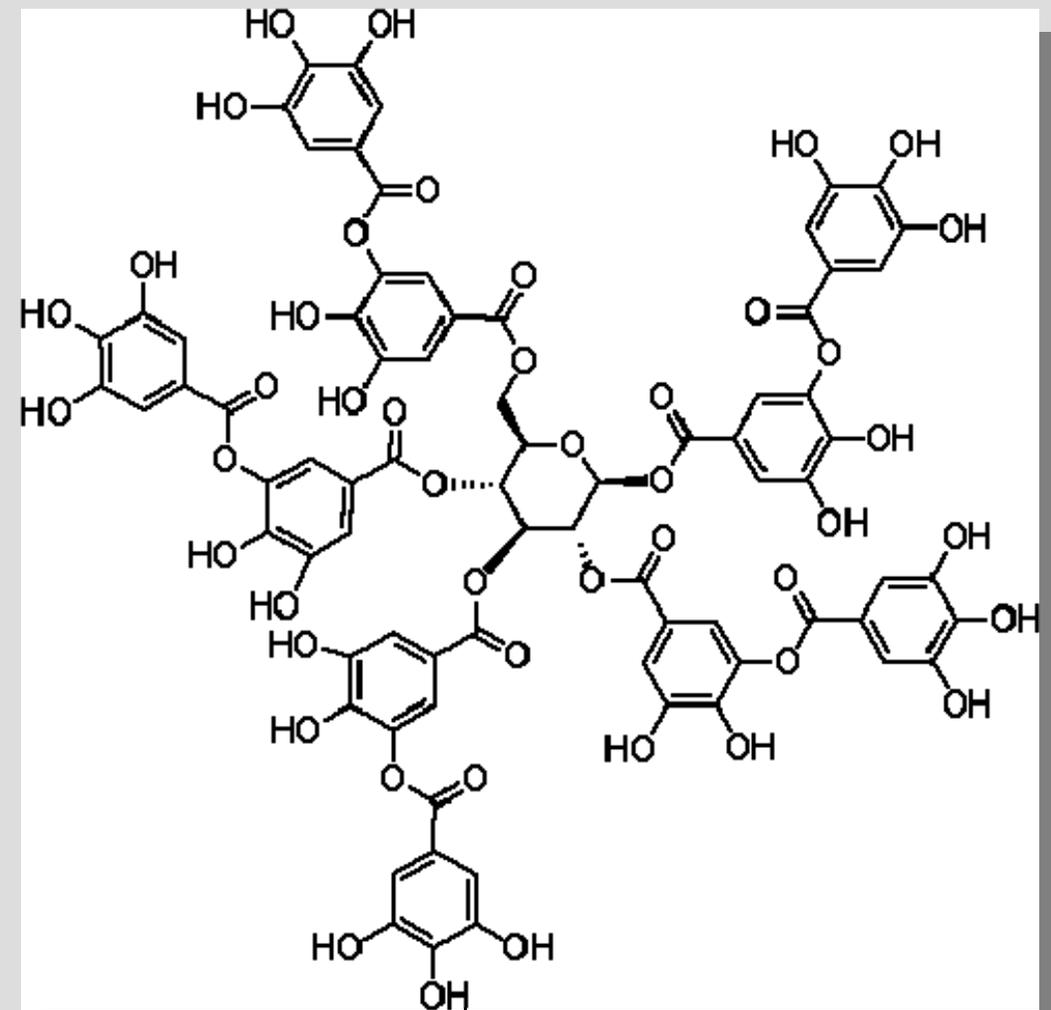
# COMMERCIAL RUST CONVERTERS

The choice of converter is very important to achieve a good result. Among commercial rust converters, a good choice is Fertan because it does not contain any polymeric compound. It's possible to dilute Fertan with ethilic or isopropyl alcohol to increase penetration rate.

Tannic acid reacts with iron oxydes to form tannates, which have bulky structures that auto-block penetration of compounds. Moreover, they remain water-soluble and could be washed away in external enviroments, so it becomes very important the presence of phosphates, since they are insoluble.

# EXAMPLE OF TANNIC ACID STRUCTURE

Tannic acid is a mixture of tannins. They form macromolecules, with a dendritic structure. Penetration of tannins solution depends on the tannin type, but normally they block penetration of forming compounds.



# SELF-MADE CONVERTERS

For museum objects, as above mentioned, it's better to use not phosphatizing converters. Normally, self-made converters contain 3-5% of tannic acid can be dilute and brushed several times on the surface to increase penetration. Penetration can be further increased by wetting the surface with water or alcohol.

It's very important to protect the iron surface with a polymeric layer after conversion, because converted oxides still remain porous and permeable to water and oxygen.

# COHESION AND ADHESION

First of all, it shall be defined the meaning of the two terms: cohesion and adhesion.

- Cohesion: when cohesion force decrease, solid materials become dusty. In these cases, it shall be used low viscosity polymeric solutions, which can penetrate into the pores. Solvents must have a slow evaporation rate to promote penetration.

- Adhesion: when adhesion between layers decrease, solid materials break down in flakes, scales, etc. A good adhesion strength is given by epoxy resins (bigger parts), but also by acrylic compounds (medium/small parts).

Also keep in mind that solvent soluble polymers give retraction due to solvent evaporation.

# CONSOLIDATION

A distinction between museum objects and external artefacts must be made and it must be also considered the difference between structural consolidation, re-cohesion of dusty layers and adhesion of some flakes or small parts.

In most cases consolidation is not reversible, so it shall be used stable compounds, which do not alterate with aging. However, the use of solvent removable polymers, such as acrylic ones, do not guarantee the complete removal on porous artefacts.

# STRUCTURAL CONSOLIDATION

On big iron objects it can be necessary to reinforce the structure with rivets, joints, etc. It's very important to select a compatible material not to create galvanic cells. As for welding or soldering, it shall be considered the heating stress of the brazing alloy on iron.

Another type of structural consolidation can be achieved with epoxy or polyester resins. Polyester resins are toxic, so it's better to use epoxy resins like EPO 150 or EPO 155. These products do not release chloride and can be considered “structural” polymers, but also hardly removable with solvents.

# FINAL PROTECTION

One of the most important step in iron preservation is final protection. The final coating must be waterproof, but also little permeable to gasses, because iron corrosion can take place also in dry enviroments (RH less than 20% ) in presence of oxygen. Acrylic resins can give protection from moisture, but a final wax coating is needed to proctect metal's surface against the gasses' permeation.

Another important parameter of polymers is glass transition temperature ( $T_g$ ), at which an amorphous solid, such as a polymer, becomes soft on heating, without liquifing. This means that a polymer like Acryloid B72 (Paraloid B72) with  $T_g$  40°C can catch the dust in external enviroments, also if no stickyness can be detected.

# ACRYLOID FAMILY

TYPE	BASE COMPONENT	SPECIFIC WEIGHT (Kg/dm <sup>3</sup> )?	VISCOSITY 25°C cPs (40% TOLUENE)?	TUKON HARDNESS AT 82°C	Tg °C
<b>Acryloid B44</b>	Methyl-Methacrylate	1,15	700 – 1700	6,5	60
<b>Acryloid B66</b>	Methyl-Buthyl-Methacrylate	1,09	210 – 345	9,3	50
<b>Acryloid B67</b>	IsoButhyl-Methacrylate	1,05	250 – 375	13,2	50
<b>Acryloid B72</b>	Ethyl-Methacrylate	1,15	350 – 650	2,9	40
<b>Acryloid B82</b>	Methyl-Methacrylate	1,16	300 – 600	3,7	35

The well-known Acryloid B72 it's only one member of acrylic resins' family. All Acryloids are termoplastic resins, soluble in ketones, esters, aromatic and chlorinated hydrocarbons. The main differences between them are:

- Tukon Hardness: higher Tukon Hardness means higher resistance of the coating to scratches.
- Glass Transition Temperature (Tg): above its Tg, a polymer begin to soft and catch the dust.

Normally, hardest resins give brittle, not very elastic coatings, but are more protective and with an higher Tg; so they are suitable for external coatings. For metals in external environments, a good compromise could be Acryloid B44 or similar acrylic coatings (i.e. Incral 44), with an high Tg (metals do heat very much) but not so hard and brittle (metals dilate with heat).

# WAXES

WAX TYPE	BASE COMPONENT	Tf °C
COSMOLLOID 80	Microcrystalline Wax	80 – 85
RESWAX WH	Microcrystalline Wax and Polyethylene Natural Wax	103 – 105
VIRGIN BEESWAX	Natural Wax	30 – 45

Waxes are different from polymers: normally it's not possible to test a wax coating hardness as they are considered easily scratchable. Melting point (Tf) can be considered an index of wax “hardness”. When heated, a wax begin to soft and, near Tf, it becomes sticky. Above Tf a wax liquify.

Obviously, beeswax cannot be used for metals in external enviroments; also in internal ones there's could be some problems, as beewax is very soft at room temperature either. Cosmolloid 80 and Reswax WH are both advisable for museum objects, for external enviroments Reswax WH is the best choice.

# COATINGS AND FINAL VARNISHES

A coating or a varnish has the function to provide a “barrier” between environment and metal.

- Museum objects: it's possible to use an acrylic varnish (waterproof, mechanical resistance) and a wax (low gas permability). Surface remains visible (transparent layers) and opaque (due to wax). Wax must be brushed on the surface to achieve low gas permability.

- External artefacts: if possible, it's a better choice to use coatings containing zinc or ferrous-micaceous inerts. These kind of products change the surface color, but provide a better protection for iron. If a transparent coating is needed, it can be used acrylic and wax. Maintenance is absolutely necessary!

# FILLERS

Filler for metals are normally epoxy or polyester resins. Two typical examples:

	<b>Araldite SV 427</b>	<b>Ara Metal</b>
<b>Colour</b>	Brown	Metallic Grey
<b>Working time</b>	40 min. - 25°C	4-8 min. - 20°C
<b>Natural Earth Addition</b>	Yes	Yes
<b>Reaction Heat</b>	Medium	High
<b>Malleability</b>	Good	Low
<b>Acrylic Retouchability</b>	Yes	Yes

# HETEROGENUOUS ARTEFACTS

Mono-material objects are easier to treat. Nevertheless iron is often one of the component of an object, coupled with stone, wood, leather and/or other metals.

- Stone: an iron or steel bar can be frequently inserted into stone buildings. Iron and stone have very different thermal expansion coefficients. This can break down the stone, leaving a vacancy all around the bar. In these cases, it can be used a filler made up with a fluoroelastomeric compound (i.e. Fluoline ST), which are sufficiently elastic to support thermal variations.

- Organic materials: wood, leather and other organic matter can release acid compounds. Acids are always dangerous for iron, so it's very important to isolate metallic parts with a barrier coating.

- Other metals: copper, gold, silver can form a galvanic cell with iron, which behave as sacrificial anode. A polymeric film can “break down” the cell, providing protection.

# SOMETHING NEW?

A very common question. New protective and inhibition systems are developed for modern steels. These systems are impossible to be applied on hystorical artefacts because they are very toxic, explosive, change permanently surface color, require heat on application, etc.

Nevertheless quite all products commonly used in restoration came from other industrial uses. Maybe it would be possible to test some of these new compounds, but time is needed to be sure of their effectiveness.

# CONCLUSIONS

Iron objects are very sensitive to environments, so a suitable solution must be studied every time for that particular situation. Actually, old experienced solutions are the more effective in iron conservation.

In conclusion, maintenance and monitoring are fundamental to preserve iron artefacts from corrosion.