

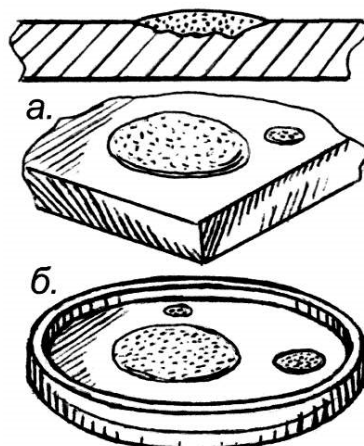
## DISEASE OF METAL ...

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This is often called corrosion, and especially iron rust. Every year, this insidious "affliction" takes away entire hecatombs of its "steel-hardened" victims. But when they call corrosion a "disease", they do not put a deep meaning into the word - it is nothing more than a beautiful figurative comparison. Metal is not a living being, and corrosion is not a biological process. And yet corrosion, like no other reaction, is similar to diseases of people and products.

Like doctors, metallurgists are fighting this "disease", "treating" the metal by injecting chemical drugs into it, protecting it with protective coatings from the penetration of a dangerous "infection", and still often turn out to be powerless against corrosion, as doctors are against other diseases. Usually, they can only helplessly watch the gradual extinction of the metal, perhaps slightly prolonging its life and alleviating suffering. Despite the seemingly good knowledge of corrosion, it continues to conceal many more mysteries. It is almost never possible to predict with confidence how a metal will behave, what kind of corrosion will develop on it, and at what speed it will proceed [1].

In this way, corrosion is fundamentally different from other chemical reactions, in which the rate and yield of products can be calculated with great accuracy, and it resembles precisely a disease - a complex biological process.



Круглые бляшки: а- окислов на поверхности металла; б- плесени и бактериальных штаммов в чашечке Петри.

*Round plaques: a- oxides on the metal surface; b- mold and bacterial strains in a petri dish.*

Let's remember the usual rust. It appears suddenly, in the form of harmless tiny foci, brown specks, but, like an epidemic, it progresses very quickly, spreading through the metal. Why does the metal not oxidize immediately over the entire surface, but corrode near the point foci of its rust infection? Chemists explain this by the fact that rusting is an autocatalytic, self-sustaining reaction, in which the corrosion products themselves are its catalysts: a grain of rust that gets on iron serves as the nucleus of an ever-accelerating and self-sustaining chain reaction of rust.

But is it possible to explain this chain contamination of the metal by the fact that rust is caused by some microbe that feeds on iron and extracts energy from its oxidation? After all, many microorganisms are known whose food is not organic, but inanimate substances: sulfur, nitrogen, hydrogen, antimony. Of these microbes, which feed on the energy of chemical oxidation reactions (initiated by them), the best known are chemobacteria. Among them, iron bacteria were also discovered that oxidize iron. So why not be microbes feeding on other metals as well? Why not assume that they are the ones that cause metal infection, its disease - corrosion, spreading like an epidemic?

So, if corrosion is just an oxidation reaction, why doesn't it occur in dry air, where there is enough oxygen? Why does intense corrosion occur only when there is moisture in the air or on the metal surface? Chemists explain this by the fact that atmospheric corrosion is an electrochemical reaction, while moisture serves as an electrolyte, accelerating such processes. But on the other hand, moisture is also necessary for bioprocesses. There is no life without water! In dry air, all microbes die or enter a state of suspended animation, hibernation. But in humid air, especially rainforests, bacteria and diseases thrive. So, maybe that's why the metal gets sick with corrosion in humid air?

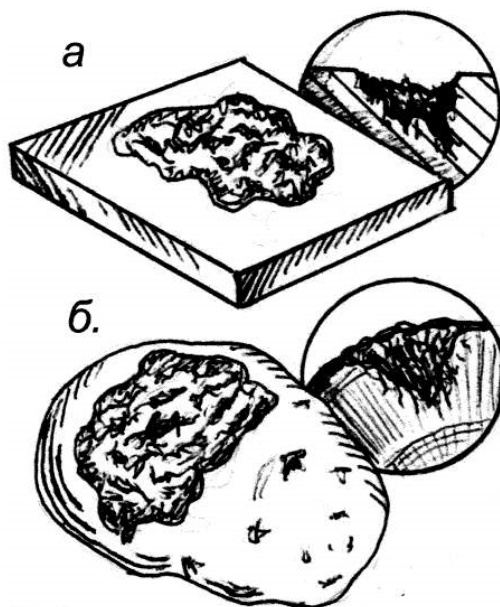
Mushrooms are especially dependent on moisture. Everyone knows how many mushrooms grow after rain. Where there is dampness, a fungus is sure to grow - mold or what is worse. Mushrooms are one of the most common, unpretentious and mysterious creatures. They live everywhere - underground, in trees, their spores are in the air. They are constantly changing, mutating, adapting. The fungus infects not only plants, animals, food, but also the walls of wooden, even stone buildings. On the other hand, it is mushrooms that we owe such vital products as penicillin, bread, beer, moonshine, etc. It is mushrooms that are most often used in biochemical industries. Micro-fungi, especially soil, yeast and mold, are some of the greatest chemists on the planet. Therefore, if any microorganism is capable of causing corrosion, it will most likely be a fungus.



Пятнышки ржавчины на железном прутке (а) и на листьях пшеницы, поражённой бурой ржавчиной (б).

*Specks of rust on iron bar (a) and on wheat leaves, affected brown rust (b).*

The very nature of metal damage during corrosion, rusting most of all resembles that found on plants affected by a fungus. There is powdery plaque, round plaques, foci of oxides growing radially, like the mycelium of a fungus (remember round spots of mold and mushroom rings in the forest), and peeling, rust scales, scars, ulcers, like in phytophthora potatoes, and uneven outgrowths, layers. These structures bear little resemblance to the usual forms of isolation of the products of chemical reactions, but they have much in common with the picture of plants affected by the fungus. It is not for nothing that our ancestors aptly christened the red noxious plaque on the golden ears of wheat caused by the fungus with the same terrible word - "rust". Apparently, they clearly saw the analogy of diseases of iron and wheat.



Рубцы и язвы на поверхности  
и на срезе: а - у металла  
при язвенной коррозии; б - у  
картошки при фитофторозе

*Scars and ulcers on the surface and on the cut: a - for metal with pitting corrosion; b -for potatoes with late blight*

Just as different plants are affected by their own kind of fungus and their own form of fungal disease, each metal "suffers" with its own kind of corrosion. Some metals are generally immune to corrosion, immune - for example, aluminum, bismuth, lead, silver, chromium. It is believed that these metals are protected from corrosion by a thin oxide passivating film on their surface. But, it is easier to explain everything by the fact that these metals are inedible and even poisonous for the corrosive fungus. It is not for nothing that the preparations of these particular metals are used in medicine as antiseptics. (Although, fungi are known that feed on aluminum, accumulating toxic heavy metals and other nasty things.) Even a thick layer of paint does not save other metals from corrosion - moisture makes its way through it.

By the way, about paints. Why do some of their types easily eliminate corrosion, while others are ineffective? An example is the well-known red lead-based paint, which, covering the bottoms of ships, perfectly protects them from rust. The point, apparently, is precisely in lead, which is toxic to most living things. Lead, present in red lead, blocks corrosion by killing germs. In the same way, some other paints do not just shield the metal, but their pigments in themselves weaken corrosion and are its inhibitors [1]. And it is not surprising: it has long been noticed that it is among the dyes that there are especially many substances with bactericidal, antiseptic properties.

In addition to painting, there are other measures to combat corrosion, including the aforementioned corrosion inhibitors - substances that inhibit the metal oxidation reaction. Among them in the first place - what do you think? - the usual formalin, known to everyone as an antiseptic and fungicide that prevents the development of fungus. And if it is difficult to chemically explain this property of formalin, then for biocorrosion it is easy: formalin kills the fungus, equally protecting metal and leather things, and regardless of the type of corrosion and metal. Formalin should be detrimental to all fungi, blocking any corrosion. All other corrosion inhibitors, in fact, are antiseptics and preservatives: chromium compounds (used for tanning leather), alkaloids (among which there are many poisons), benzoic acid salts (a well-known antiseptic, which are so rich in cranberries and lingonberries).

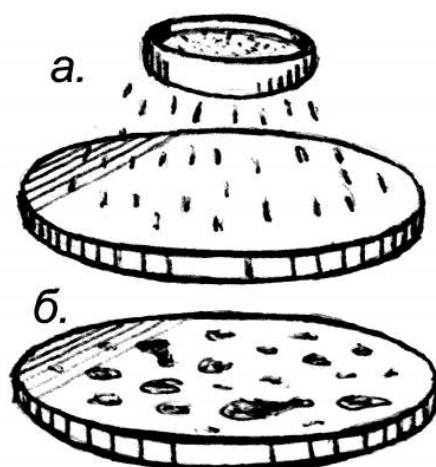
But do not let what has been said make the reader think that corrosion is a purely biological process. No, corrosion is primarily a process of chemical oxidation of a metal. In its pure form, it creates oxide films, goes intensively in aggressive environments, in the contact of dissimilar metals, in the presence of current (electrocorrosion). However, at low temperatures and in a neutral environment, chemical corrosion is very slow. The role of microbes is to accelerate this natural process thousands, millions of times by influencing the reaction with special biological catalysts - enzymes, or enzymes, in order to use the energy of the oxidation process. So harmless chemical corrosion, with the assistance of microbes, turns into a terrible devourer of metals.

Everyone observed the difference between the rate of chemical and biological oxidation on the example of wood. Even without heating, the tree gradually "burns", oxidizes in air, but so slowly that it would take thousands of years for it to completely decay. But it is worth moistening a tree with water, or placing it in a humid atmosphere, as it, like metal, will oxidize without residue in a few years, decay under the influence of microorganisms that settle in moist wood and accelerate decay. By releasing enzymes, these microbes impart a small, but necessary activation energy to the reaction, so to speak, an invested capital, which brings them a much larger profit when the launched reaction gives up energy. Sometimes this energy release caused by microbes is so powerful that rotting substances ignite spontaneously.

It is interesting that in chemistry textbooks, the processes of rust formation on iron objects, food assimilation by the body, decay, aging of rubbers and oils are often cited as an example of such initially sluggish slow combustion reactions [2]. And it seems that in all these examples it is biological oxidation that takes place, as in the case of rotting and digestion, by the way, also proceeding with the assistance of microbes. For example, the aging process of rubber, which becomes sticky or brittle from time to time, has a lot in common with corrosion. Like it, the aging of rubber,

once starting at one point, like a disease, quickly spreads in all directions, being transmitted by contact.

It turns out that the aging of rubbers, rubber, latex is decomposition under the influence of microbes - probably not a fungus, but bacteria. It is not for nothing that bactericidal substances - alcohol and phenol (carbolic acid) - are used as anti-aging additives introduced into rubber, which give fresh rubber the smell of a medical cabinet and tar. Microorganisms can feed on both the rubber itself and the sulfur atoms that cross-link it. And the oil is unlikely to go rancid under the influence of oxygen alone. Surely, microorganisms are involved in this process. It is quite possible that the notorious antioxidants used in the fight against diseases, aging of materials and people do not block oxidation itself and free radicals, but the vital activity of microbes that support this oxidation.



Высев культуры микробов на металлическом диске или его спонтанное заражение окислами (а) создаёт вскоре очаги точечной и язвенной коррозии (б).

*Sowing a culture of microbes on a metal disc or its spontaneous contamination with oxides (a) creates soon foci of pitting and pitting corrosion (b).*

But back to metal diseases. There is one among them that, it would seem, has nothing to do with corrosion: they are related only by the similarity of "symptoms." We are talking about the "tin plague". It is known that after frost, simple white tin can begin to turn into a gray powder - into gray tin, which has a different crystal structure. This process is called "plague" for a reason: if at least a grain of gray powder hits the metal, the "tin plague", like an epidemic, will instantly cover the entire metal. There is no longer any oxidation here, but the very mechanism of "contamination" is very typical for corrosion and disease. So here, too, our ancestors were not mistaken, calling the process "tin plague", if it really is caused by microbes that are pathogenic

for the metal, drawing energy from the decay initiated by them, the transformation of tin. The book [3] tells about the tin plague and how it is fought with it in an interesting way: "Scientists have learned to make tin "grafts" that provide the metal with immunity against the "tin plague". A suitable "vaccine" for this purpose is, for example, bismuth. Bismuth atoms, supplying additional electrons to the tin lattice, stabilize its state, which completely excludes the possibility of "disease"".

If the "tin plague" is caused by microbes, then the quotes can be safely omitted here, because it will be a real disease, and bismuth grafting will have a biological, and not a chemically stabilizing effect. Moreover, bismuth and its preparations are known as a strong antiseptic agent that kills microbes and can literally be a medicine against tin plague. Likewise, alloying of iron - the introduction of an impurity, for example, chromium, into it - greatly weakens corrosion. As in the case of bismuth, "grafting" with toxic chromium compounds should reduce corrosion by inhibiting the vital activity of microbes. But there are substances necessary for microbes, on the contrary. Therefore, "dirty" metals are less resistant to corrosion. Thus, iron contaminated with sulfur rusts very quickly. But such corrosion, which occurs in solution, is probably no longer caused by fungi, but by sulfur bacteria, which convert sulfur into sulfuric acid, which corrodes the metal. This is exactly how, with the help of acid, microbes often destroy metal, stone, walls of buildings.

Of course, these ideas are too unfamiliar to be taken on faith (although science already recognizes the existence of microbes that contribute to the development of corrosion). Therefore, direct experiments are needed to verify them. You can, for example, put a piece of iron in a Pasteur flask filled with water vapor, and, after igniting it over fire (in order to kill microbes), check after a while whether rust appears on the iron. If it is absent, or very little, it will prove that under normal conditions it is microorganisms that cause corrosion. Their destruction either completely stops or greatly slows down corrosion.

It is even better to try to directly identify the causative agents of its disease among the oxides and rust on the surface of the metal using an optical or electron microscope. So, what remains is to wait for a new Pasteur who will discover these very pathogens and find a means of dealing with them, reducing the "mortality" of metal products. Pasteur's example is very instructive, because before him, scientists believed that all diseases have chemical causes, arise from a chemical disorder of the body. And only Pasteur proved that most diseases have their own pathogen, their own microbe (even such diseases as ulcers, cancer, atherosclerosis are now associated with viruses and microbes). It is interesting that for the first time he discovered the causative agents of the disease not in living beings, but in substances, in complex chemical compounds - beer, wine, vinegar. And the first pathogens of fermentation and diseases that he encountered in fermentation vats were precisely fungi - yeast and

mold. Before Pasteur, fermentation and spoilage of products were explained by purely chemical reasons, as is now corrosion. So, it is worth thinking about the biological nature of diseases in other man-made substances and materials: metals, rubbers, plastics.



*Corrosion microbes, devouring metal*

Our world is literally permeated with microbes: they float in the air, in the stratosphere, live in land, water, they thrive and are active even in hot volcanic craters, in nuclear reactors, in the cold snows of Antarctica. They are able to receive energy from anything - from heat, light, from chemical ones, and it would not be surprising if also from nuclear reactions (see, for example, V. Krupin's book "Dwarfs give birth to giants"). Perhaps it was microorganisms that created a natural nuclear reactor in Oklo, accumulating radionuclides there. It is possible that microbes have long mastered cold nuclear fusion.

The role of microorganisms, as before Pasteur, is still greatly underestimated. There is no doubt that it was they who made the Earth what it is, that microbes should be considered not only as destroyers, but also as creators. Nowadays it is admitted that even the weather on Earth is caused by bacteria (see "Engineer" 2005 No. 2, 2006 No. 4). And if microbes can destroy metal, it is even more likely that they once created it in the form of ore [4]. The hypothesis of V.I. Vernadsky that deposits of metal ore, coal, oil were created by microbes that processed the initial raw material and concentrated it in deposits (this is how elements and some fungi and plants accumulate).





*a - Yeast fungus; б - sprouted from mycelium spores of the fungus of bread rust; в - tree-like structures from bacteria "cases".*

For example, there is good reason to believe that the huge deposits of iron-manganese nodules lying right on the seabed were created by microbes living in the water [3]. Similar microbes, probably, form a plaque on the stones in the form of a bronze "tan" containing a lot of iron and manganese (some iron bacteria deposit manganese compounds in addition to iron). Many people could see a film of rust on the marshes, created by "case" iron bacteria. Dying off, "cases" of iron bacteria accumulate at the bottom of reservoirs in the form of the so-called swamp ore. Ancient swamps could have been giant biochemical reactors producing fossils. It is not for nothing that metal inclusions, nuggets, their tree-like structures, like those of corals, give the impression of something created by wildlife. So, tales about gnomes, tiny creatures collecting underground riches and hiding them in the pantries of the earth, may turn out to be true if these tiny creatures are understood as microorganisms [5]. At least some oil and sulfur deposits are already seriously considered by scientists as the waste products of microbes.

Modern fairy tales - science fiction, depicting the capabilities of microbes - also no longer seem fiction [4]. More than once it spoke about microbes that transform naked lifeless planets, creating soil, landscapes and deposits of minerals, about microorganisms eating plastic and metal. That is why a real fairy tale is beautiful, that over time, the thoughts expressed there can turn into reality. Note that even the first science fiction writer, Jules Verne, in the novel "Children of Captain Grant", noted the analogy of rust and disease, pointing out that in Australia, where

natural conditions prevent the development of microbes, not only people, but also metals are a little sick: iron in the air does not rust.

So, if it is possible to identify the causative agents of the disease of metal and other materials, then not only all the oddities of corrosion will be immediately explained, but also new ways of dealing with it in the form of coatings, "grafts", additives containing modern antiseptics and antibiotics that can give the metal "immunity" - corrosion resistance. A metallurgist, a developer of alloys, will then also have to become a physician, a microbiologist, to deal with the treatment and prevention of metal diseases. Perhaps, then, finally, it will be possible to cope with the epidemic, which takes away millions of tons of metal every year, with a disease called corrosion. But it is possible to put such microbes in the service of man, forcing them to destroy waste, garbage, purify drains and air, extract new materials, as is often done, albeit on a limited scale. For example, microbes are already being used in so-called bacterial hydrometallurgy to extract inaccessible metal. They even removed bacteria that absorb gold from the water. It remains to be hoped that they will serve humanity, and not the lovers of easy money, suffering from a "metal disease" of a completely different kind.

*S. Semikov*

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