Materials • Mechanics • Physiology • Engineering • Aerodynamics

BIKE TECH

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MATHEMATICAL ANALYSIS

The Effect of Winds on a Bicyclist's Speed

Osman Isvan

A cyclist's sense of wind can be very different from the actual wind conditions. The perceived or apparent wind is a combination of the relative air velocity felt by the moving cyclist and the additional air movement—the wind—that is sensed even when standing still. Air drag is determined by this combined wind.

The combination plays tricks with your perception, so that the true effect of wind—especially wind from the rear quarter direction—can come as a surprise. This article is a mathematical exploration of how wind affects the ground speed of the cyclist, and of how the cyclist will perceive the wind speed and direction from his moving vantage point.

We will assume in this article that the terrain is flat, the cyclist's power output is constant, and that all the cyclist's power is expended to overcome air drag. This constant power assumption introduces a unique feedback loop that affects the cyclist's final speed into the wind: a change in the wind speed and/or direction results in a change in the bike speed which, in turn, results in a change in the apparent wind, the actual input.[1]

Head Wind

Let's consider a specific case of a cyclist that generates a power P, and rides at a speed c, in still air. When riding into a

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[1] *Tire rolling resistance and mechanical losses are assumed small and are not included in this discussion. This assumption lessens the accuracy of this discussion at low power outputs. However, as you'll see, final bike speed is normalized with respect to no-wind bike speed, so only the change with speed of these two drag factors is ignored at higher power outputs. Therefore, the results of this discussion become more accurate as power output increases.*

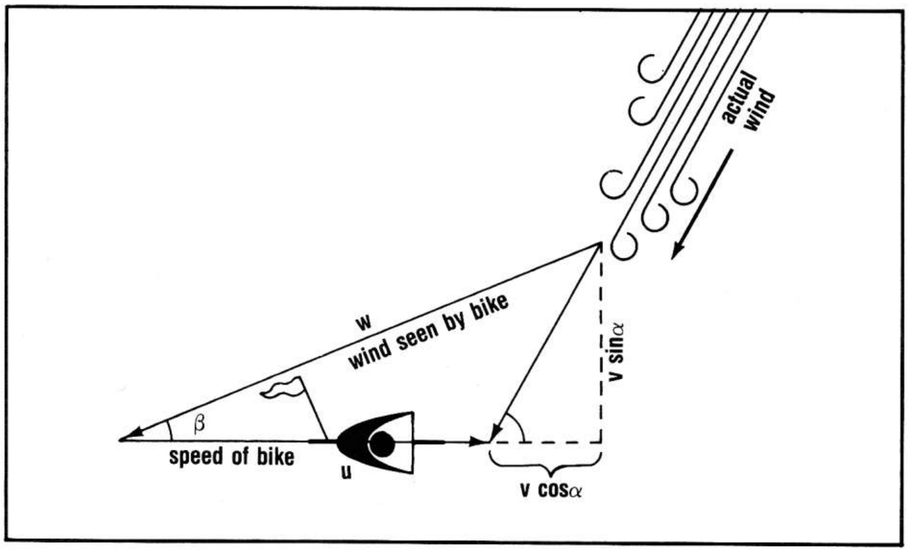

Figure 1: The velocity vector triangle.

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- Have you ever ridden your bicycle on a windy day and sworn that no matter what direction you head, you're fighting a head wind? Your perceptions are correct, says Osman Isvan. In fact, you'll learn that even tailwinds become headwinds in Isvan's mathematical presentation of "The Effect of Winds On a Bicyclist's Speed."

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- Imron® paint has earned a reputation in the bicycling world as a tough, durable paint that offers good corrosion protection. What makes Imron® such a good paint and how does it protect your steel frame? In the first of a two-part article, "Painting with Imron®," frame painter Les Lunas discusses the chemistry of corrosion and how paints are formulated to combat it.

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- Mario Emiliani concludes his series, "Can Surface Finish Affect the Strength of Your Frame?" with a comprehensive discussion of chrome plating. Chrome plating looks good and wears well, but trouble may lurk beneath its hard surface. Chrome causes no problems, but the application process can.

headwind that has a ground speed *v*, this cyclist will actually ride at a ground speed *u* $(u<c)$. Thus, the apparent wind speed will be $u + v$. The problem presented in this article is to find the cyclist's speed *u* as a function of the wind speed *v*.

Air-drag power for a cyclist is the product of the drag force and the cyclist's speed. Since drag force is proportional to the square of the apparent wind speed, the air power against the wind is proportional to the product of the apparent wind speed squared and the cyclist's ground speed. For constant power output this relationship is expressed as:

$$u(u + v)^2 = c^3$$

(see appendix for derivation). (1)

The unknown *u* is a real positive root of equation 1. In polynomial form, equation 1 is

$$u^3 + 2vu^2 + v^2u - c^3 = 0. \qquad (2)$$

Before elaborating on the roots of this equation, which is for headwinds only, let's further generalize the problem by introducing another parameter, the wind angle α. If the wind has an angle α with respect to the direction of the cyclist's travel, as shown in Figure 1, then the moving cyclist senses an apparent wind speed *w*, and an apparent wind angle β.[2]

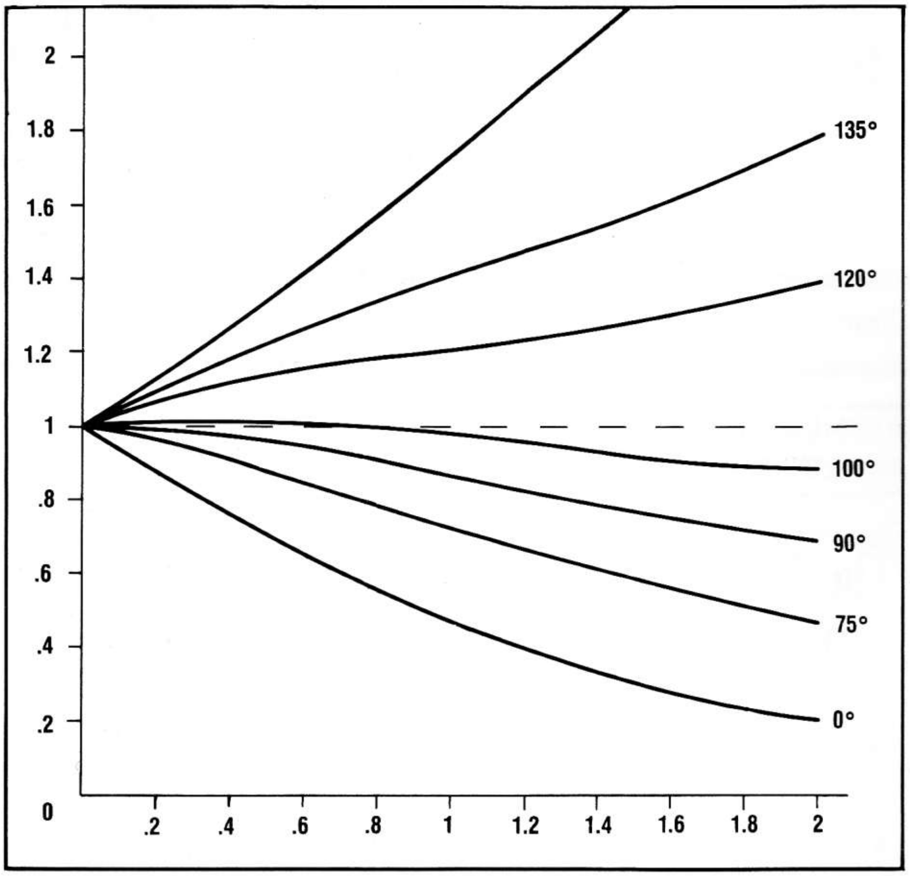

Figure 2: Bike speed at different wind conditions. Bike speeds and wind speeds are normalized by dividing them by the "base case" no-wind bike speed, c.

George Retseck

With these generalized parameters, an expression for drag force will be proportional to:

$$w^2 \cos \beta. \qquad (3)$$

By replacing the drag force expression $(u + v)^2$ in equation 1 with 3, the constant air power equation becomes:

$$u(w^2 \cos \beta) = c^3. \qquad (4)$$

From Figure 1 we see that,

$$w^2 = (u + v \cos \alpha)^2 + (v \sin \alpha)^2, \qquad (5)$$

(by the Pythagorean theorem)

and,

$$\cos \beta = \frac{u + \cos \alpha}{w}.$$

Note that both *w* and β are related to *u* and cannot be expressed in terms of *v* and α only. Substituting equations 5 and 6 into 4 and simplifying, we obtain the expression:

$$\frac{u(u + v \cos \alpha)}{\sqrt{(u + v \cos \alpha)^2 + (v \sin \alpha)^2}} = c^3. \qquad (7)$$

When both sides are squared and the algebra is carried out, equation 7 becomes:

$$u^6 + A_5u^5 + A_4u^4 + A_3u^3 + A_2u^2 - c^6 = 0 \qquad (8)$$

where,

$$A_2 = v^4 \cos^2 \alpha$$

$$A_3 = 2v^3 \cos \alpha\ (1 + \cos^2 \alpha)$$

$$A_4 = v^2\ (1 + 5\cos^2 \alpha)$$

$$A_5 = 4\ v \cos \alpha.$$

For different combinations of wind speed and wind angle (*v* and α), the bike speed *u* for constant aerodynamic power can be found as a real positive root of equation 8.[3] I did this, with the aid of a microcomputer, and graphed the results in Figure 2. The bike speed *u* and the wind speed *v* are non-

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[2] *For equation 3, I'm assuming that the effective frontal area and the drag coefficient change with wind angle in such a way that their product is a constant. For a shape as irregular as a person on a bicycle, this assumption is debatable.*

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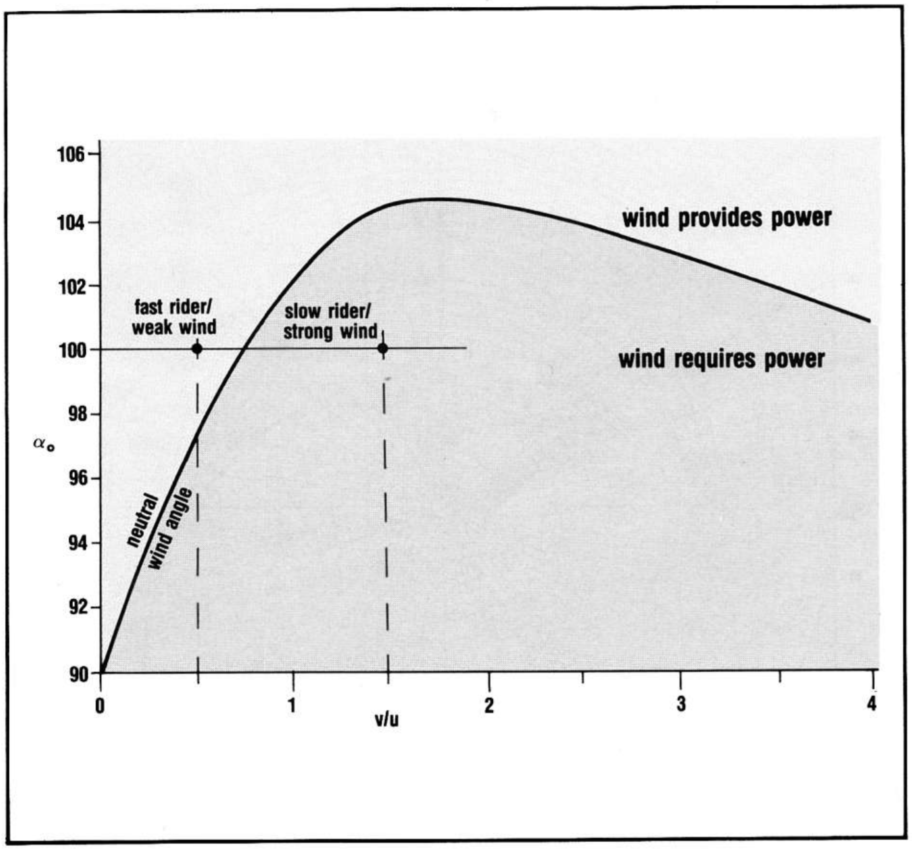


Figure 3: At wind angles around 100 degrees, the wind can either require or provide power depending on the wind speed/bike speed ratio *v/u*. The wind has no effect on any speed ratio that falls on the neutral wind curve.

dimensionalized in Figure 2 by dividing them by the still-air bike speed, *c*. (For the rest of this article, wind speed and bike speed will be normalized against the "base case" speed *c*.)

Note that the curve for $\alpha = 100°$ in Figure 2 intersects the dashed line $u/c = 1$ at $v/c = 0.75$. This means that at this angle, a cyclist rides faster with a mild wind ($v < 0.75\ c$) than without one, yet a stronger wind from the same angle forces the bike speed to drop below the no-wind value. Another interpretation is that for a given wind speed, riders with higher power output (so that their base speed *c* is more than 4/3 the wind speed *v*) are helped by the wind while slower riders are fighting against it. This situation occurs only at wind angles around 100°.

Figure 2 also shows that wind angles equal to or less than 90° always add air drag, and wind angles somewhat above 100° always help the rider. But wind from angles in between can go either way. It seems strange that wind from certain angles can sometimes help and sometimes hinder progress, but the mathematics, not common sense, bear this fact out.

Neutral Wind Angle

Let's define a quantity called the neutral wind angle, α_o, which is a wind angle that has no effect on bike speed. This angle is a function of the wind speed/bike speed ratio *v/u*, and satisfies the equation for drag force that results in the bike speed *u* equal to the still-air bike speed *c* ($u = c$). The equation for drag force felt by a moving rider is:

$$F = kw^2.$$

Since we are concerned with air drag only in the direction of motion,

$$F_x = F \cos \beta = kw^2 \cos \beta.$$

The condition of the neutral wind angle is satisfied when,

$$F_x = ku^2, \text{ with } u = c.$$

So,

$$kw^2 \cos \beta = ku^2$$

or,

$$w^2 \cos \beta = u^2. \qquad (9)$$

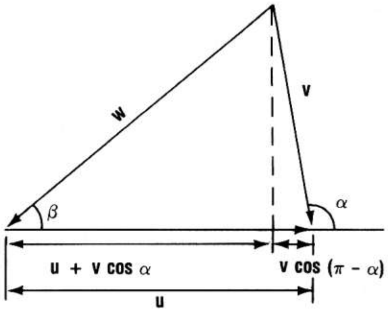
Satisfying equation 9 in terms of the wind values α and v is done by substituting,

$$w^2 = u^2 + v^2 + 2uv \cos \alpha$$

and

$$\cos \beta = \frac{u + v \cos \alpha}{w},$$

derived from the figure below.



Equation 9 yields a maximum value for α_o of 104.7° at $v/u = 1.8$. This means that winds from angles greater than 104.7° always help the rider go faster. We've seen that winds from angles less than 90° always hinder. The effects of the intermediate angles are graphed in Figure 3; they either require or provide power depending on which side of the neutral wind curve the point plots.

Note that this dependency involves not only the wind speed but also the bike speed. As in the case of wind from an angle of 100 degrees, faster riders may benefit from a wind that slower riders have to fight against. But with strong winds from the same direction, the opposite is possible.

Average Speed

So far, we've found results for rides taking place in straight lines, but most roads aren't straight. However, if a ride starts at a point A and ends at Point B, the angle of the path of the bicycle to the wind averages out to be equal to the angle between the wind and the straight line AB. This fact results in the average speed of the ride being fairly close to the speed of riding on the straight line AB, especially if most of the ride is in that general direction.

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[3] *Descarte's Rule of Signs shows that for 0° < α < 90°, equation 8 has only one real positive root, but that for 90° < α < 180°, it has either three positive roots or one. All results presented here reflect the greatest of the three roots. The other two roots account for the condition that with a tailwind, as well as riding downhill, a rider can ride at two additional forward speeds by applying power in the reverse direction.*

If we extend this reasoning to an out-and-back route that is fairly direct and subject to a steady, unshifting wind, then we can draw some interesting conclusions about the average speed $\overline{u}$, and about the effect of wind angle on total trip time. If the upwind leg of the trip is ridden at speed u_1 and the downwind leg at speed u_2, then the average speed for the entire route is computed from,

$$\overline{u} = \frac{2u_1u_2}{u_1 + u_2}$$

(see appendix for derivation).

Figure 4 shows the dependence of u and $\overline{u}$ on the wind angle for the particular case of the wind speed v equal to the still-air bike speed c. Speeds for the out-and-back legs are read as radial distances from the center of the figure to the intersection of the speed curves. An example of upwind and downwind speeds of a cyclist riding first into a wind 30° to the side and then returning with a 30° tailwind is shown.

For higher wind speeds, the upwind/downwind speed curve becomes increasingly eccentric; but as the wind speed approaches zero, all speed curves converge to the circle of radius one (shown as a dashed line), which is just the cyclist's speed in any direction under no-wind conditions.

Note that the variation of the average speed due to wind angle (eccentricity of the average speed curve) is small compared to its deviation from c, meaning that the speed of the wind is a more important factor on round trip time than is its angle. This applies to all wind speeds less than c. But as wind speed increases past c, the wind angle becomes the dominant factor in average trip speed.

Note also that for moderate tailwinds ($90° < \alpha \lesssim 102°$), the bike speed is less than the still-air bike speed. (This fact is in keeping with the results of the earlier discussion on the effects of wind from angles around 100°.)

The average speed curve in Figure 4 has maximum values at wind angles of 90°. It turns out that this is characteristic of all average speed curves for out-and-back routes at all wind speeds. This leads to the conclusion that for an out-and-back time trial, the fastest times result when the wind is blowing at an angle of 90° to the course. This result holds regardless of the wind speed or the bike speed (see the accompanying sidebar, "Circular Routes").

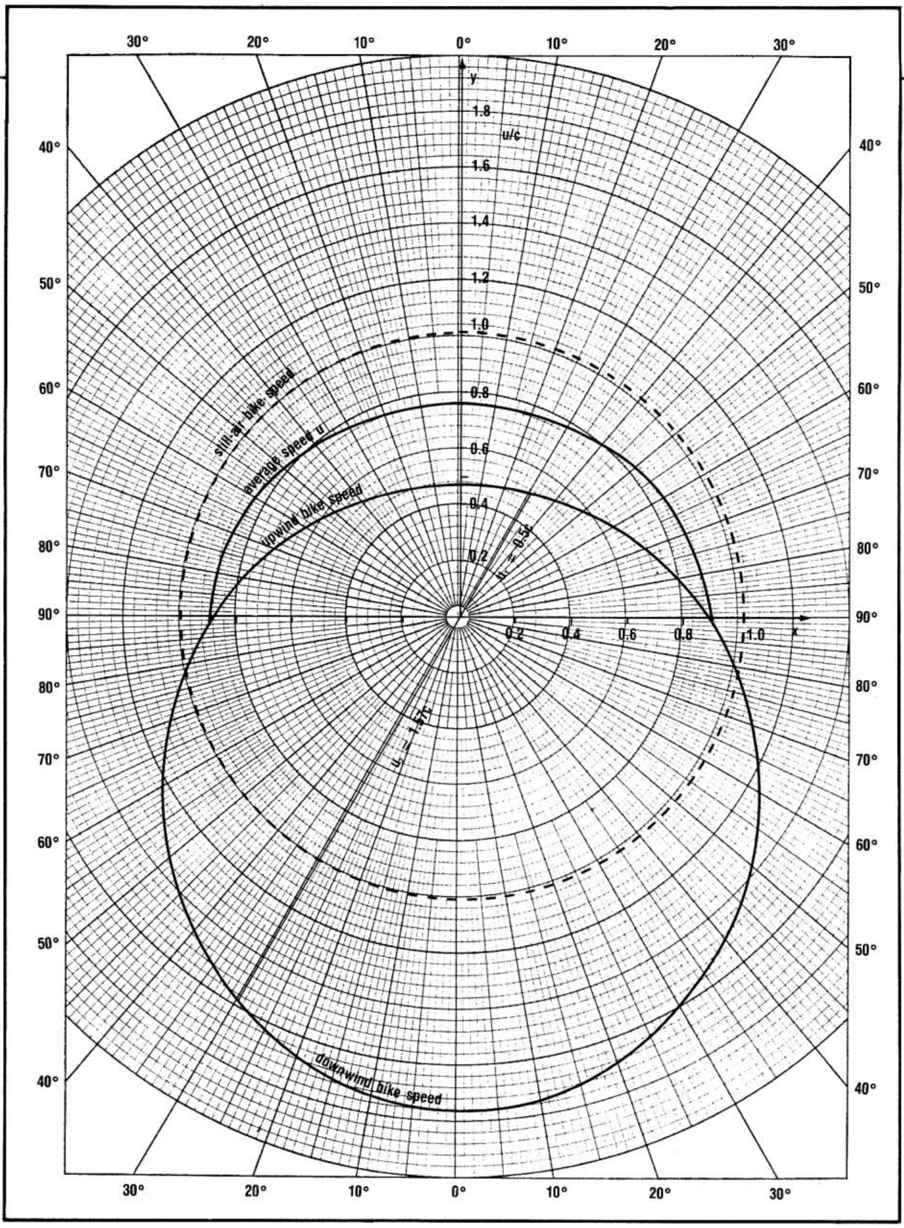

Figure 4: Bike speed and round trip average speed as a function of the wind direction at constant wind speed v/c = 1.0. Speeds are measured as radial distances from origin to plotted curves.

George Retseck

Tacking

Figure 4 also demonstrates that a straight line, being the shortest distance between two points, is also the quickest way to cycle (although not the fastest), even head-on into the wind. The increase in speed achieved by "tacking" into the wind (assuming the roads allow this sort of maneuvering) is not enough to make up for the extra distance traveled.

This fact can be observed from Figure 4 as follows: assume that the wind is blowing in the $-y$ direction (i.e vertically downward); in the worst case, the cyclist's destination will be in the $+y$ direction. Since the radial distance from the origin to the curve labeled "upwind" represents the bike speed in that radial direction, the perpendicular distance from the x-axis, being equal to $u \cos \alpha$, represents the distance traveled per unit time in the y direction.

The quickest route to a point straight upwind of the cyclist is, then, to go where this vertical is a maximum, thereby maximizing the upwind component of his or her speed and then turn toward the destination at the halfway point. Figure 4 shows, however, that this maximum upwind component coincides with the radial minimum at zero degrees. This is the case for all wind speeds checked. Note also how little trip time is lost by first visiting another place before cycling toward the destination, even up to 30° out of the way.

Perceived Wind

With an idea now of the effect of the wind on bike speed, it remains necessary to examine the direction and speed of the wind as perceived by a rider. Figure 5 shows the variation of the apparent wind in response to the real wind for four different power levels. This figure reveals why the bicyclist's perception of winds leads to the belief that,

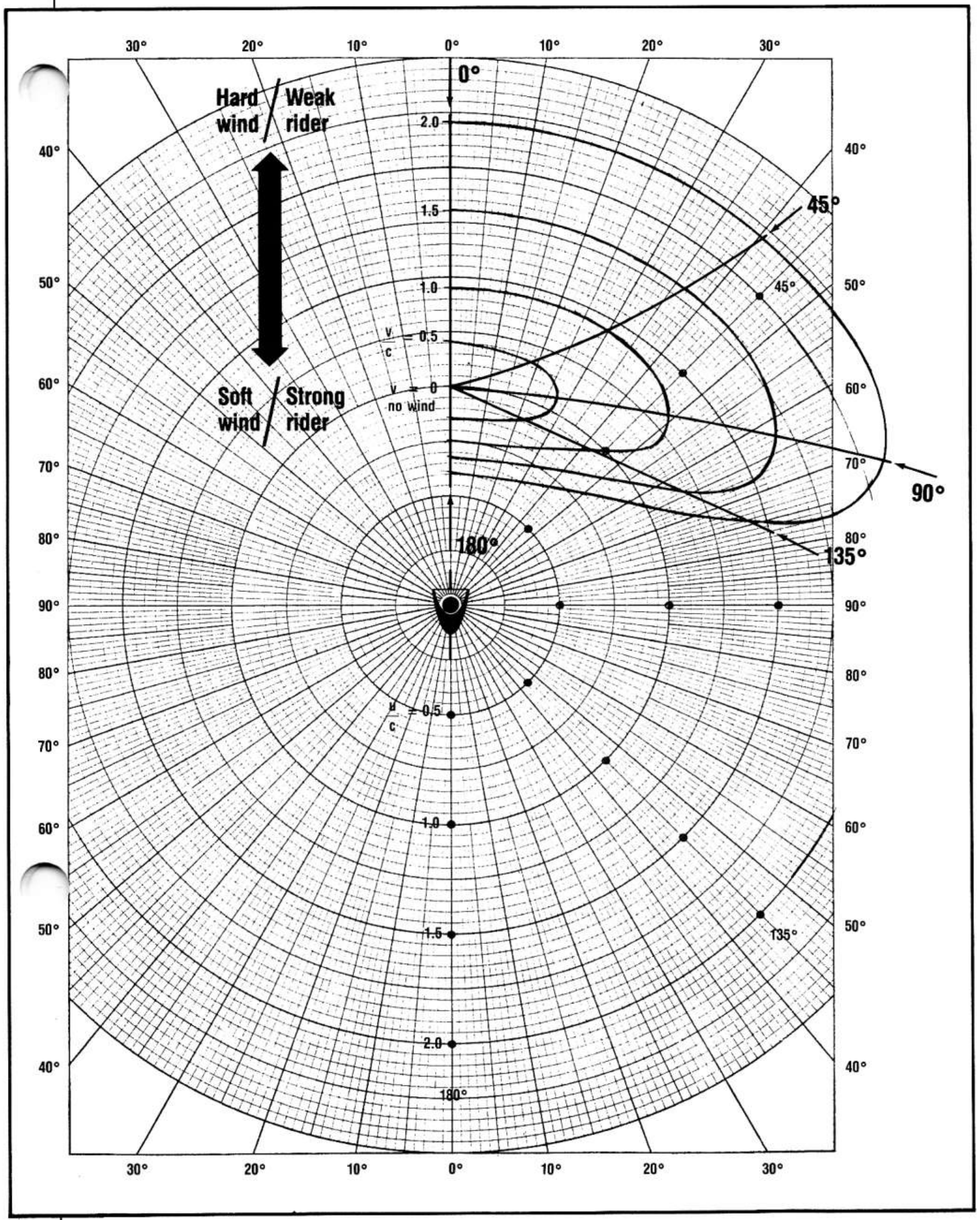

Figure 5: Relation between apparent wind and actual wind, or why every wind feels like a headwind. Black (distorted) coordinates indicate true magnitude and direction of wind; gray coordinates show the strength and direction apparent to the rider in the middle of the figure. The black pattern was generated from the gray pattern by displacing each point by a distance corresponding to the bicycle speed which would result for that wind condition, assuming for each curve that a constant amount of power is devoted to overcoming air drag. As a result, bicycle ground speed can be read on this graph as the distance between a position on the black pattern and its corresponding position on the gray pattern.

All wind speeds (shown as radial distances) are given in terms of c, the speed that the bicycle would go in no-wind conditions.

"I'm always riding against the wind." What actually happens is that one naturally tends to increase speed until the sensation that one is riding against the wind occurs.

Note that for a strong rider or a gentle wind ($v/c = 0.5$), even side winds and tailwinds appear as almost direct headwinds, although tailwinds do increase speed. For a typical example of $c = 12$ mph and $v = 6$ mph, Figure 5 shows that the apparent wind angle never exceeds a shallow 28 degrees and the apparent wind speed is no less than 10 mph even for a perfect tailwind. A 12 mph wind coupled with the same rider effort will give wider apparent wind angles, but the wind will still appear faster than 12 mph up to a wind angle of 135°, or 75 percent of all possible wind angles. Even as a tailwind, this apparent wind hits the rider's face with a relative speed of nine mph.

Rules of Thumb

It seems, then, that when it comes to predicting the effects of wind on a cyclist's speed, common sense is sometimes fooled. The facts emerge only with a careful mathematical analysis and are best visualized with careful graphing as in Figure 5. But for casual reference, these "rules of thumb" should keep your mind occupied the next time you go for a ride on a windy day:

- The apparent wind is never from behind nor even close to the side; rather it usually appears to come from a shallow angle toward the face at fairly high speed.
- Tacking into the wind (even if the roads allow) doesn't work with bicycles as it does with sailboats. A straight line is always the quickest path to your destination, even in a direct headwind.
- Cross winds from 90° will slow you down unless you pedal harder.
- Winds between 90 and 105° may provide or require extra power depending on your bike speed. Winds between these angles generally hinder weak riders and help strong ones. Winds from further behind help all riders.
- For an out-and-back time trial on a straight course, no wind is best, but cross winds are better than head- or tailwinds. The more oblique the course is relative to the wind, the shorter your total time will be.
- The total time to complete a circular loop is independent of wind angle; it depends only on wind speed (see the sidebar, "Circular Routes").

Appendix

(P)ower = Drag force × Bike Speed

For no-wind conditions,

Drag force = $\frac{1}{2} \rho C_D Ac^2$
(ρ = air density; C_DA = effective frontal area of bike/rider.
Let $\frac{1}{2} \rho C_DA = k$).

Bike speed = c.

For wind conditions,

Drag force = $k(u + v)^2$
and bike speed = u.

So, power consumed by air is:

$P_{\text{no-wind}} = kc^2c = kc^3$,

and

$$P_{wind} = k(u + v)^2 u.$$

For constant power output,

$$P_{wind} = P_{no\text{-}wind}, \text{ so}$$

$$k(u + v)^2 u = kc^3,$$

or

$$(u + v)^2 u = c^3.$$

$$\text{Average speed} = \frac{\text{Total distance}}{\text{Total time}}$$

$$= \frac{2d}{\frac{d}{u_1} + \frac{d}{u_2}} = \frac{2d}{\frac{u_2 d + u_1 d}{u_1 u_2}}$$

$$= \frac{2u_1 u_2}{u_1 + u_2}$$

Circular Routes

So far we have seen how the wind affects the ride speed on straight lines and out-and-back routes. More complex routes can be approximated as a combination of straight lines, so that when the times for each leg of the ride are calculated separately and added together, the total time and the average speed of the total ride can be found. For a given power, this is generally a function of both wind speed and wind angle.

Rides that end where they began (closed loops) are of particular interest to bicyclists. The approximate loop of such routes is a polygon. For equilateral polygons, the dependence of the total time on the wind angle is a periodic function, oscillating between minimum and maximum values as the wind becomes perpendicular to a side or bisects a corner. For example, a 40-mile ride, 10 miles east, 10 miles south, 10 miles west, and 10 miles north can be completed in minimal times when the wind is from the north, east, south or west; conversely, the longest times are required for wind directions out of the northeast, northwest, southeast and southwest. This means that for a square-shaped route, as the wind is rotated 360 degrees around the route, the ride time goes through four maxima and four minima. This is not a matter of coincidence but a direct result of the symmetry of the problem.

Similar results are obtained for all equilateral polygons. As can be expected, the difference between the longest and shortest times for given wind speed decreases as the number of corners and sides of the polygon is increased. A particularly interesting and useful consequence of this fact is that at the limit, when the route approaches a circle, the total ride time becomes independent of the wind angle. This is because, regardless of the wind direction, an equal infinitesimal distance is covered at all angles relative to the wind. Therefore, for a closed circular loop, the average speed $\bar{u}$ for given power is a function of wind speed only (see Figure 1). The data points for Figure 1 are obtained from a 16-sided equilateral polygon.

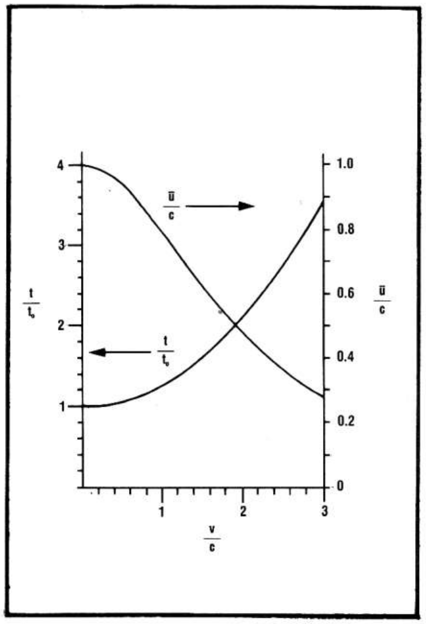

Figure 1. The total time t, and the average speed $\bar{u}$, to complete a closed circular loop at constant power, plotted against the wind speed v. Constants c and t_o are the no-wind bike speed and the no-wind total time on the circuit, respectively.

Unfortunately, the procedure from which Figure 1 is derived does not produce an analytical function. But a visual inspection of the graph of t/t_o immediately suggests that a parabola may nicely fit the curve. In fact, it does. The equation,

$$\frac{t}{t_o} \approx 0.3 \left(\frac{v}{c}\right)^2 - 0.05\left(\frac{v}{c}\right) + 1,$$

has less than one percent error in the given range. Although this is only a truncated power series representation of the actual function and does not reveal the nature of the physical relations involved, it is nevertheless a practical substitute.

For a less accurate, more practical rule of thumb, if a near-circular closed loop is in question, ignore winds that are much slower than your no-wind bike speed. For wind speeds close to it, add 25 percent to your no-wind time. For stronger winds, up to a factor of 2.5, multiply the no-wind time with that factor. For example, if a 100-mile long circle is completed in 10 hours with no wind, a 10 mph wind will require 12.5 hours; a 20 mph wind will require roughly 20 hours, if the same effort is maintained.

Osman Isvan

MATERIALS

Painting With Imron®, Part I: Corrosion of Metals

Les Lunas

Les Lunas knows a great deal about painting bicycles; he used to paint framesets for Bruce Gordon. Lunas's bread and butter was DuPont's Imron®, a paint that has gained a reputation among framebuilders and their customers as a tough, chip-resistant enamel that holds up well to the rigors of cycling.

What makes this paint so good? Lunas will share his knowledge about the qualities of this wonder paint, and will relate his experiences on applying and maintaining a good paint job.

But paint does more than make a frameset look good; it also provides a barrier between the metal and moisture that would corrode it away. In this first installment of a two-part series, Lunas explores how and why metals corrode, and how paint and other coatings work to keep corrosion under control. This review of corrosion chemistry will lay the goundwork for Part II, which will explain how to avoid corrosion with the correct materials (particularly DuPont Imron®) and painting technique.

Nature of Corrosion

Some metals are found in nature in metallic form. These metals, including gold, silver, and platinum, are called noble metals; they are mined and put to use with very little refining and remain relatively unaffected by their environment. But other metals, like copper, aluminum, zinc, iron, and tin exist in nature bound to another nonmetallic element in a chemical compound. Much energy and expense are required to extract these metals from their natural compounds and refine them into useful materials.

Corrosion is a chemical reaction in which refined metals revert to a more stable state. Such metals corrode when attacked by some element in their environment that unites with these metals to form stable compounds, and in the process, releases the energy gained during the refining process.

All metals normally used to make a bicycle—steel, aluminum, and titanium—will corrode in the normal environment. For this reason, much research has been done to develop paints and other protective coatings to seal these metals from the corrosive environment.

A protective coating is effective if it blocks or controls the chemistry of corrosion. Three categories of coatings exist: painting, plating with a noble or sacrificial metal, and anodizing. Anodizing is good protection for aluminum and titanium; steel can be plated with a nonreactive metal like chrome or nickel. But for a number of reasons, most steel bicycle frames are painted. Paint provides good corrosion protection, is inexpensive to buy and apply, and comes in a myriad of good-looking colors.

Electrochemistry

The corrosion of metals is an *electrochemical* reaction, which is a chemical interaction between two substances that occurs during an exchange of electrons. Electron exchange occurs because one substance has many free electrons that are weakly bound to the atomic nuclei; the other substance has a great affinity for these electrons. This reaction occurs in an electrochemical *cell,* which is an electrical circuit with a positive and a negative electrode that are electrically connected and immersed in a conducting medium called *electrolyte.*

The negative electrode, or *anode,* is the site in the cell in which one substance, usually a metal, is attacked by some element(s) in the electrolyte. The anode dissolves into the electrolyte and ionizes by losing one or more electrons; these electrons flow through the electrical connection to the positive electrode or *cathode,* because they are attracted by the second substance, usually another metal or a gas. The dissolved positive ions in the electrolyte then migrate to the cathode because they are attracted to the negatively charged electrons (opposite charges attract). Once at the cathode, these ions will either combine with the second substance or else attach themselves to the cathode's surface (see Figure 1).

This electrochemical reaction occurs spontaneously when all the components of the cell are assembled because the affinity for electrons at the cathode is strong. The strength of attraction is measured as a cell voltage; the higher the voltage, the quicker the reaction occurs. The reaction will continue until either the anode dissolves completely or changes in the electrolyte increase its internal resistance, and ions no longer form and migrate to the cathode. Once ionization ceases, electron flow stops and the cell is "dead."

Chemists call this electrochemical reaction a redox (reduction-oxidation) reaction. When the anode dissolves and loses electrons, it is considered oxidized; the substance that gains the electrons at the cathode is said to be reduced.

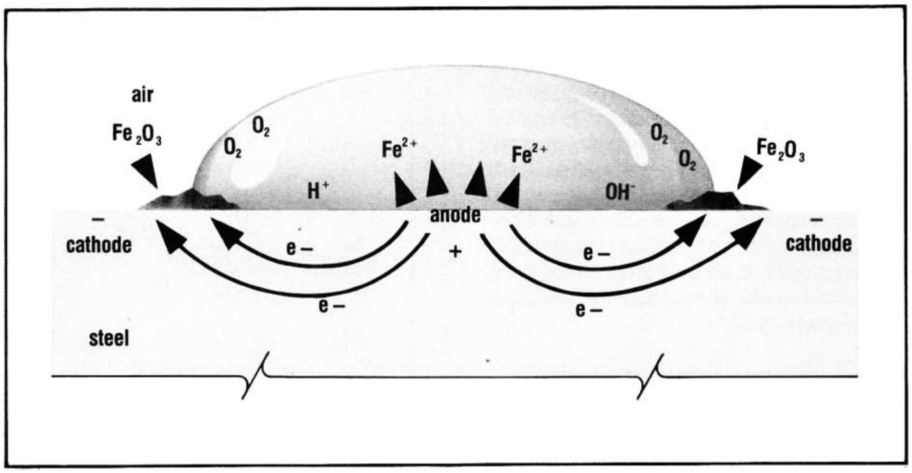

Figure 1: Water drop on steel depicting corrosion cell. Electrons and positive iron ions flow out of the anode. The electrons migrate to cathode and reduce oxygen and hydrogen; iron ions combine with oxygen in solution and form rust.

George Retseck

Making Oxides

Most metals will corrode under normal atmospheric conditions—the presence of moisture and oxygen is all that's required. Although water is blamed for corrosion, it is actually the dissolved oxygen and hydrogen ions (from acids) in the water that are responsible. Without these two dissolved gases in the water, the corrosion reaction proceeds very slowly or not at all because metal atoms will not be ionized.

The rate of the corrosion reaction depends on the environment of the metal. A high concentration of acid in the water speeds the dissolution of metal ions; salt in the water lowers the electrical resistance of the electrolyte and allows the metal ions to migrate more quickly to the cathodic areas, so rust forms more quickly. High temperatures also speed the electrochemical reaction.

The end products of metal corrosion are oxides. For instance, iron and oxygen react to form iron oxide, commonly called rust. Although the corrosion processes of metals are similar, the extent of corrosion among metals differs. Nickel corrodes only slightly, and its oxide appears only as a tarnish. On the other hand, rust is very noticeable and steel will continue to corrode until all of it is converted into rust. Aluminum and titanium are actually more reactive to oxygen than iron, yet their oxides are generally less visible and are usually less damaging than rust. Some aluminum alloys will corrode to the stage where they become susceptible to low-level stress cracking. This phenomenon is called stress-corrosion cracking.

The differences in how much metals will corrode in the normal environment lie in how the oxides of each metal bond to the parent metal. Aluminum and titanium oxides bond tightly; after a surface layer is built up, they become barriers to further corrosion by shielding the parent metal from oxygen attack. (This is why aluminum and titanium are anodized. Anodizing corrodes these metals in a controlled way, building up a thick, protective layer.)

On the other hand, iron oxide does not bond tightly to iron, so it flakes off easily, exposing a fresh steel surface to renewed attack. Also, as we'll see below, the oxidation of iron is a two-stage process in which the end product of corrosion is deposited away from the area under attack. As long as steel remains exposed to water, corrosion will continue and, eventually, structural damage will be done.

Since steel corrodes in the normal environment more severely than other frame building materials, and since all the frames I painted were made of steel, I will focus the rest of this article on the corrosion and protection of steel.

Corrosion of Steel

The corrosion of steel begins when water contacts the steel surface (for a more complete description of the corrosion process, see "The Chemistry of Steel Corrosion" sidebar). A corrosion cell is established under the water drop with the anode of the cell under the drop and the cathode out at the edges. (The positioning of these electrodes corresponds to the oxygen concentrations within the water drop: the area under the drop is relatively oxygen-poor compared to the oxygen-rich edges. Because a redox reaction requires that oxygen be reduced by gaining electrons, any flow of electrons from one area toward an area with oxygen defines the positioning of the anode and cathode. Electrons will flow away from an anode into a cathode.) The iron atoms under the drop begin dissolving into the water with a simultaneous loss of two electrons; the relinquished electrons migrate to the cathodic edges, where they reduce oxygen into various other molecules, mostly water (see Figure 1).

After the iron ions are in solution, a second step brings the corrosion process to completion: the iron is oxidized once more by giving up another electron; it's then attracted to the negative cathode where it combines with the oxygen molecules to form the stable compound, iron oxide. These oxide molecules accumulate on the steel surface where they build up into the scaly, reddish material called rust.

Controlling Rust

The corrosion of steel is slowed or stopped by coating it with some material which intervenes with one of the steps of the corrosion process. Such a coating can limit corrosion in one or more of these three ways:

—Limit exposure of the steel to atmosphere

—Control the oxidation reaction at the anode

—Employ a reverse redox reaction

Nickel and chrome plating are relatively non-reactive to moisture and provide good protection for steel. Proper plating techniques are important though; if these metals are applied too thin (in the case of chrome, less than one-half micron thick), they will be porous and will not prevent corrosion of the steel beneath. (See Mario Emiliani's article on chrome plating in this issue for more details about proper plating techniques.)

One drawback with plating, however, is that any scratch through the plating down to the steel can lead to serious corrosion problems. This is so because there's an electrode potential between the plating metal and the steel; this potential accelerates electron flow out of the steel, aiding the the ionization and dissolution of iron atoms. This condition leads to a deep pit in the steel (see Figure 2).

Paint is somewhat permeable to water and oxygen, so it is important not to let water stand for too long on a painted part. This is not usually a problem on a bicycle with a good paint job that is not left out in the rain, but some areas are prone to rust even on a well-maintained bike—those areas under clamps and bands used to attach components to the frame. Water will be drawn under these parts by capillary action and, if not evaporated, will eventually seep through the paint and rust the tube beneath.

(Some frames that came into my shop for repainting that had clamps for down tube shifters and cable guides would show raised paint beneath these clamps and bands of rust on the tubes after I stripped the paint away. For this reason, I recommend the liberal use of frame braze-ons.)

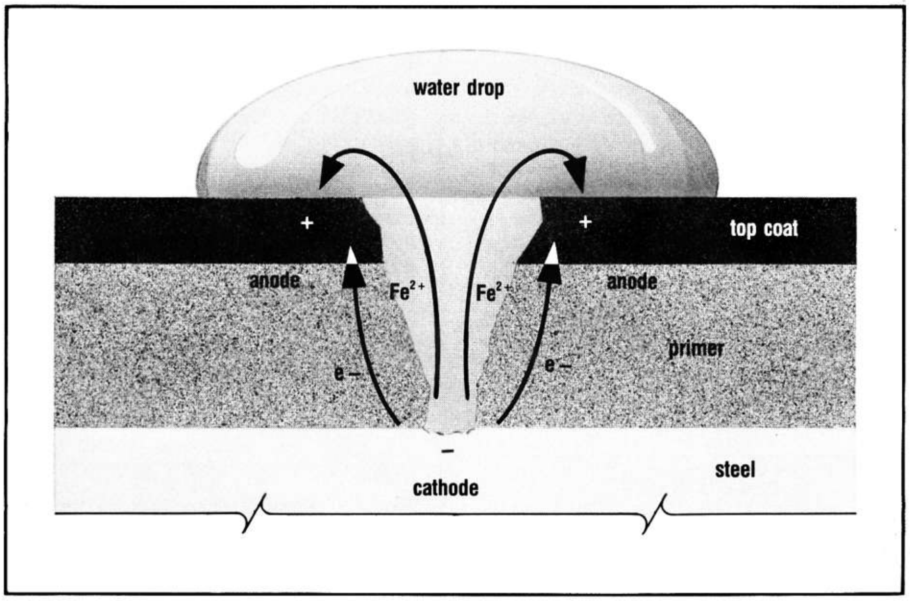

Figure 2: Pitting corrosion. A scratch in the paint or metal plating forms a small corrosion cell. The base of the pit is the anode; the edges, the cathode. Metal atoms ionize at the anode and go into solution, causing pit to deepen. Prevention requires sealing the scratch with touch-up paint or some other protective coating.

George Retseck

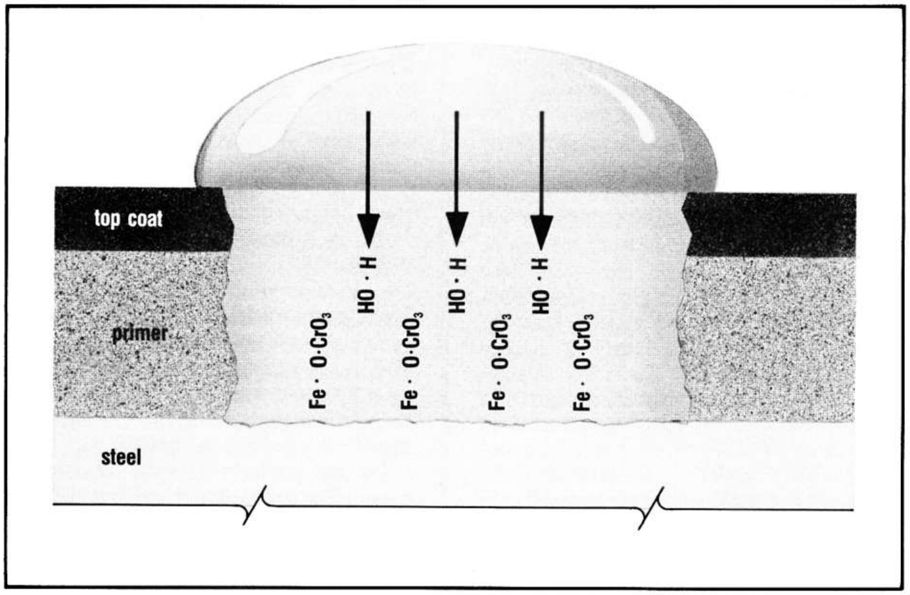

Figure 3: Inhibitive corrosion protection. Chromates in paint bond with iron ions, forming an oxidation layer that insulates the iron surface from oxygen attack.

By adding anti-corrosive ingredients to paint, it can be fortified to fight rust. These ingredients are effective by either controlling or reversing the redox reaction. Normally, these ingredients are added to the primer or undercoat; the top coat offers only a measure of water repellency and improved appearance.

Inhibitors

The ingredients which control the redox reaction are called passivators or inhibitors. We know that under normal corrosion conditions, the oxides of steel are formed at a site separate from where the iron ions are dissolved. Inhibitors do their job by forcing the corrosion reaction to begin and end at the same location. Manipulating the reaction in this way results in the iron oxide's bonding securely to the iron surface; thus, in this case, rust acts as a sealing agent, similar to the oxide protection on aluminum and titanium. Once a thin oxide layer is formed on the steel, the corrosion reaction ceases be-

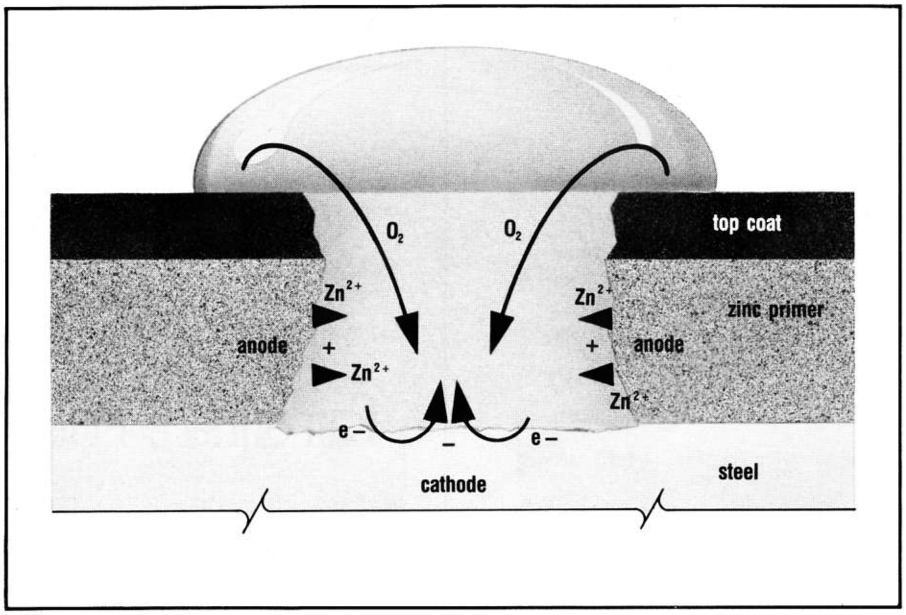

Figure 4: Sacrificial corrosion protection. A coating like zinc is more reactive than iron to oxygen, so *it* corrodes rather than steel.

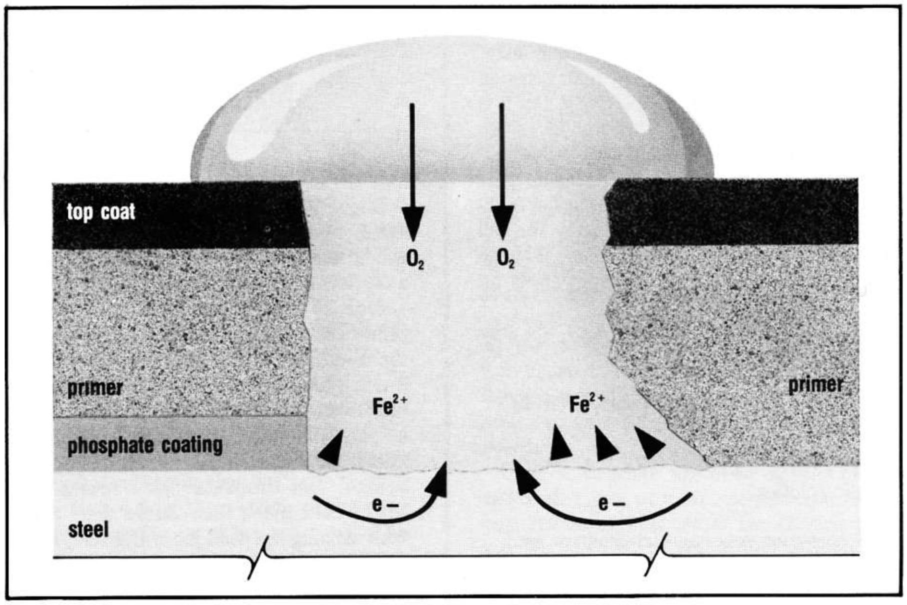

Figure 5: Phosphate coating limits electrons to attack oxygen, so corrosion proceeds slowly. Without phosphate protection, corrosion will form and undercut good paint, causing blister.

cause the layer electrically insulates the metal.

Chief among the inhibitors are the chromates, which are chromium compounds added to primer paints. Chromates will dissolve as negative ions with any moisture that passes through the top coat into the primer. These ions drift down to the metal and, being highly polar[1], will align and bond their negative ends with the positively charged iron ions. A reaction occurs that separates the oxygen molecules from the chromium; these oxygen molecules then bond with the iron molecules, forming iron oxide. Also, some of the chromium bonds with oxygen in the water to form chromium oxides which deposit on the steel surface.

This on-site formation of rust and chromium oxide forms an effective barrier that prevents continued iron oxidation (see Figure 3).

Chromate primers are especially protective because they continue to work throughout the life of the paint. Should the oxide layer break, more chromates will filter down, go through the above reaction, and re-seal the oxide layer. This self-healing ability will continue until the chromates are exhausted. For this reason, it is important to apply a thick primer coating.

(This inhibitive action is why stainless steels don't visibly corrode. Stainless steel contains 13 percent or more chromium as an alloy; in a process similar to the reaction above, the chromium builds a protective oxide layer on the surface.)

Sacrificial Protection

Another type of protective primer, zinc powder in primer paint, works in the same way as the zinc coating applied when galvanizing steel: more electrochemically reactive than iron, the zinc oxidizes rather than the iron, hence the "sacrifice." The zinc readily oxidizes when permeated by water, providing the electrons to reduce the oxygen. The zinc acts as the anode in the corrosion cell and the steel becomes the cathode. The electrochemical effect is to reverse the redox reaction, because steel is a receiver of electrons rather than a donor (see Figure 4). Since no iron atoms are ionized, no iron ions will dissolve into the water.

This type of primer has to be painted directly onto the steel because a good electrical connection is necessary to allow electron flow between the zinc and the steel. Otherwise, both metals will corrode.

Zinc primers continue to offer a margin of protection even when scratched. If water contacts the scratch, the zinc, rather than the steel, will provide the materials for corrosion. Zinc-primed steel will corrode, but at a slower rate than without the zinc. Once the zinc is exhausted, iron corrosion will commence as usual.

Phosphating

An excellent non-paint coating that helps protect steel is a phosphate coating. Phosphating is a pre-paint treatment in which clean, uncorroded steel is dipped or washed in a solution of zinc, manganese, or iron phosphate. The reaction between the acidic phosphate solution and the steel causes phosphate crystals to grow on the surface. These crystals bond tightly with the steel, and as they are electrically nonconductive, electrons will not be attracted out of the steel.

Phosphate protection really helps when there are breaks in the paint, because it limits the availability of electrons to the attacking oxygen. Without it, the corrosion will proceed under the paint. This effect is seen

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[1] *Polar molecules have positively and negatively charged ends.*

on areas of the paint that have been chipped or scratched. If the steel was not phosphate treated, a blister of paint will form around the scratch as the corrosion proceeds to eat the metal underneath the paint (see Figure 5).

Phosphating provides temporary protection between the time a frame is brazed and cleaned and when it is painted. The phosphate crystals also provide a good surface for paint to adhere to.

When painting steel for maximum corrosion protection, it must first be thoroughly cleaned of all surface rust and grease. Next, a phosphate coating is applied, followed by a coat of primer paint. The top coat is the final moisture barrier and, as we'll see in Part II of this article, is also the primary defense against bangs and scrapes that could put chips or scratches into this multi-layered protection.

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The Chemistry of Steel Corrosion

The corrosion cell modeled in the main article is called a differential-aeration cell because there are different concentrations of dissolved gas at the two electrodes. This difference in oxygen concentration provides the impetus for electrons to migrate from the oxygen-poor anode under the water to the oxygen-rich cathode at the edges.

The rate of the redox reaction is influenced by the amount of dissolved salts in the water, its acidity, and by other impurities in the water. Dissolved salts aid the movement of ions by lowering the resistance of the electrolyte; acid in the water contributes H^+ ions which accelerate the reduction reaction at the cathode.

Let's consider some simplified chemistry of the corrosion process as two half-cell reactions:

The dissolution of iron in the water at the anode is,

$Fe \rightarrow Fe^{2+} + 2e^-$,

standard reduction potential, $\epsilon° = +0.41$ volts.

The reduction of oxygen (and some hydrogen in an acidic solution), is either,

$\frac{1}{2}O_2 + H_2O + 2e^- \rightarrow 2OH^-$ (basic solution; $pH > 7$), $\epsilon° = +0.41$ volts or,

$\frac{1}{2}O_2 + 2H^+ + 2e^- \rightarrow H_2O$ (acidic solution; $pH < 7$), $\epsilon° = +1.23$ volts.

The full-cell reactions will be either,

$Fe + H_2O \rightarrow Fe^{2+} + 2OH^- + \frac{1}{2}O_2$, $\epsilon° = +0.81$ volts

or,

$Fe + 2H^+ + \frac{1}{2}O_2 \rightarrow Fe^{2+} + H_2O$, $\epsilon° = +1.64$ volts.

Since the reduction potentials are positive, these reactions will occur spontaneously. The higher potential in an acid solution drives the reaction more vigorously. But it is important to realize that the potential values are correct only for specific concentrations[2] of dissolved gases in the cells. At lesser concentrations, for instance, the corrosion reaction "runs" at a slower rate because the cell voltages are less. This means, then, that the pH of the electrolyte will have an effect on the cell potential value.

Once in solution, the Fe^{2+} ions will lose another electron,

$4Fe^{2+} + 4H^+ \rightarrow 3Fe^{3+} + 2H_2\uparrow$, (acidic solution)

$4Fe^{2+} + O_2 + 2H^+ \rightarrow 4Fe^{3+} + 2OH^-$, (basic solution).

The corrosion reaction end-product, rust, is formed by,

$4Fe^{3+} + 6O^{2-} + xH_2O \rightarrow 2Fe_2O_3 \cdot xH_2O$.

Other products form in lesser amounts, primarily FeO, Fe_3O_4, and FeO(OH).

The beginning and end products of this reaction are identifiable, but there are many intermediate compounds that form temporarily in the solution as the cell "runs," that have not yet been identified.

Other than the iron oxides, water, and various hydroxyls, heat and an increase in entropy are by-products of corrosion, the inevitable adjuncts of a system reverting to a more stable state.

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[2] *These conditions are specified in any introductory chemistry text in a Standard Reduction Potentials table.*

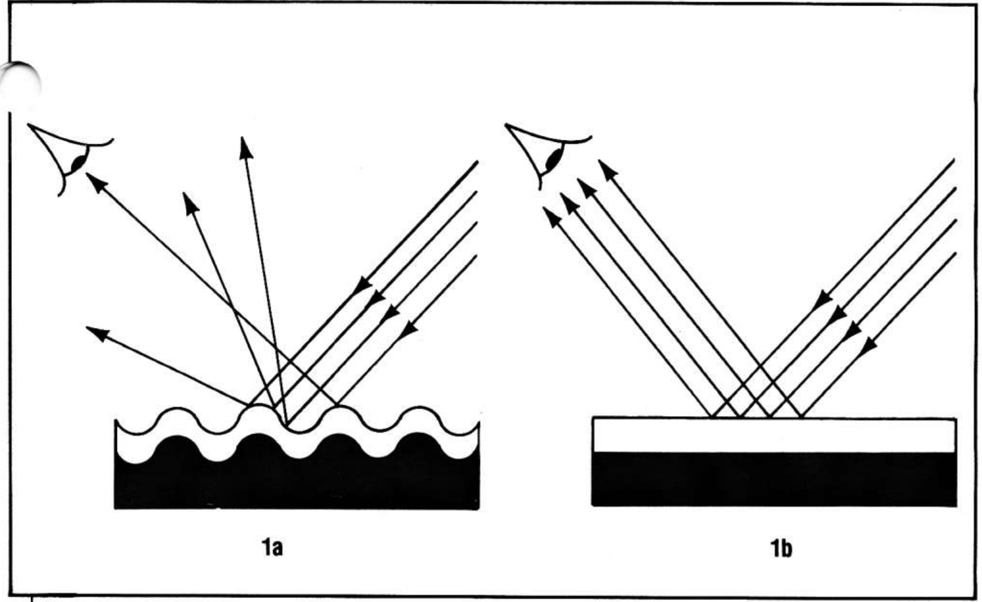
MATERIALS

Can Surface Finish Affect the Strength of Your Frame? Part III: Chrome Plating

Mario Emiliani

There are numerous ways to protect steels from rusting. The easiest and most widely used method is painting. Paint acts as a barrier to oxygen and moisture, two of the necessary ingredients for corrosion. But paints can chip off easily, exposing steel to the atmosphere. Steel bicycle frames must live in a tough environment; inept mechanics (and even good ones!) can ruin hundred-dollar paint jobs with a slip of a tool, chains inevitably slap chainstays when riding over bumps, and dropouts can't retain paint. There isn't much that can be done to prevent marring the paint job with a tool, but the latter two problems can be prevented by coating these vulnerable areas of the frame with a harder and more chip-resistant substance, such as metal plating.

The application of a thin coat of another metal onto a steel frame is accomplished by a process called *electroplating.* Metals are hard, and electroplated metals adhere strongly to the base metal, since metal-to-metal bonds are formed. But the choice of metals is important. For example, it wouldn't make sense to plate dropouts with copper because it's too soft and would quickly wear off. In addition, copper tarnishes. Chromium, however, is a much harder metal and is therefore well suited for wear resistance. Chrome plate also remains bright and is easy to care for. Because of these advantages, chrome plating can be used as an alternative to paint on some areas of the frame.


1a

1b

Figure 1: Chrome plate tends to reproduce the surface texture of the substrate. An irregular substrate results in a dull looking plate because some of the light rays aren't reflected back into your eyes (Figure 1a). Chrome plated onto a smooth substrate appears much brighter (Figure 1b).

George Retseck

Surface Preparation

Before a frame can be chrome plated, its surface must be thoroughly cleaned to provide a suitable substrate to which chromium ions can easily attach themselves. Thus the frame, or portions of the frame to be plated, must be free of rust, grease, and brazing flux for maximum adhesion. If this isn't done, the chrome plate will blister and/or peel off.

For cosmetic reasons, the surfaces to be plated must also be relatively smooth. Chrome tends to follow the contours of the surface to which it's plated. Figure 1a shows an irregular substrate that has been chrome plated. Notice how the surface of the plate matches the contours of the substrate. This can be a problem because a rough plated surface appears dull since some of the light hitting it isn't reflected.

But there is no need to have extremely smooth substrates, because very small surface irregularities actually improve adhesion by mechanically locking the metal plating onto the substrate and providing more surface area. Certain chemicals added to the plating bath can make the chrome plate smoothly over small surface irregularities by inhibiting plating on hilltops but allowing valleys to become filled. Bicycle tubes, if they haven't been particle blasted, gouged with files, or roughened by wire brushing, are normally quite smooth. So surfaces to be chrome plated need only be fine sanded and lightly buffed in preparation for plating.

The next step is to remove residual buffing compounds and other oils and greases. This is usually done by placing the surfaces to be plated in an agitated alkaline solution[1] which is maintained at about 60° C (140° F). The frame is left in the tank for about three minutes, then placed in an acid bath to remove oxides (rust, etc.). Typically, platers use dilute (~ 10 percent) sulfuric or hydrochloric acid at about 55° C (130° F). The immersion or tank time varies depending on the amount of cleaning needed, but usually runs between three to ten minutes. This process is known as *acid pickling,* and is widely used because it is cheap and effective. Between the alkaline and acid cleaning steps, there is usually a series of rinses to avoid contaminating the solutions.

Once the surface has been cleaned of oils and oxides, one or more metallic undercoatings can be applied before the chrome plating. Frames may be plated first with copper or nickel, or both, because these surfaces provide good adhesion and a smooth substrate for the chromium atoms to plate to, and they provide an extra measure of corrosion protection.

Electroplating

To enhance our understanding of the electroplating process, which is electrochemical in nature, let's take a quick look at the general nature of the electrochemical reaction. An ordinary dry cell battery (e.g., a flashlight battery) is a classic example of an electrochemical cell. The cell consists of an anode, a cathode, an electrolyte, and an electrical connection between the anode and cathode. If any one of these four ingredients is missing, electrochemical reactions won't occur.

The anode is simply the portion of the cell that dissolves (corrodes) under some action of the electrolyte. When this happens, each metal atom loses a few electrons[2] which are conducted to the cathode because the anode and cathode are in electrical contact. The result is a flow of electrons from the anode (or positive electrode) to the cathode (or negative electrode). A battery continuously produces a flow of electrons when electrical contact is made between the anode and cathode. When all of the anode has dissolved away, the battery is dead. This illustrates how electricity (or flow of electrons) is created by chemical reactions.

As more and more electrons flow to the cathode, an electrical charge imbalance develops in the electrochemical cell. That is, the cathode has an excess number of negatively charged electrons, while the electrolyte contains a large number of positively charged ions. Since oppositely charged particles attract each other, ions move toward the cathode and attach themselves to it in order to regain the electrons they lost at the anode. Thus, ions from the anode plate onto the surface of the cathode and remain there because they are now stable (i.e., they have equal numbers of protons and electrons).

Figure 2a shows a cross-sectional view of a dry cell battery. The cathode is the carbon core, the zinc case is the anode, and the electrolyte is a moist chemical paste (usually ammonium chloride). When contact is made between the anode and cathode, the zinc case begins to dissolve into zinc ions and two electrons (Fig. 2b). The electrons flow to the cathode, lighting up the bulb along the way. At the same rate the anode is dissolved, zinc ions plate onto the cathode (Figures 2c and 2d). This portion of the electrochemical reaction is called electroplating.

The reason why electrons must flow from the anode to the cathode is that the carbon rod is more ***noble,*** that is, it has a much lower tendency to dissolve into carbon ions compared to zinc. Stated another way, electrons flow from the anode to the cathode as water flows from high ground to low ground. It's not possible for the opposite to happen unless energy is added (i.e., water will go uphill only when pumped).

Electroplating occurs by the same principle as in the dry cell battery: metal ions form at the anode and migrate to the cathode where they plate. However, steel has a

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[1] *Alkalines are the chemical opposites of acids.*

[2] *Atoms are made up of particles called neutrons, protons and electrons. Neutrons have no electrical charge, but protons have a positive charge and electrons have a negative charge. Stable atoms have equal numbers of protons and electrons to maintain electrical neutrality. Ions are atoms that have either extra or too few electrons, so they can have either a net negative or positive charge.*

greater tendency to dissolve (i.e., it's more anodic) than many of the metals that are commonly plated on it. For example, imagine we wanted to plate copper onto steel. If steel were the anode and copper the cathode, as in Figure 2a, steel (actually iron) would plate onto copper. But this is the reverse of what we want! To remedy this, copper is made the anode and the steel frame is made the cathode. This is done by reversing the direction of electron flow with the help of an external source of electricity. In other words, the steel frame is made more noble relative to the copper by adding energy to the electrochemical cell. This is what happens in principle.

In practice, anodes are sometimes used which don't dissolve to supply the cathode with metal ions. Instead, the metal to be plated on is contained in the liquid electrolyte in small concentrations. The anode, which can be a completely dissimilar metal (for example, lead), simply provides a surface whose energy is high enough to transform metal atoms in solution into metal ions (a process known as ionization). These ions then plate onto the steel cathode. The electrolyte must be replenished periodically with metal atoms. This is the case in copper, nickel, and chrome electroplating.

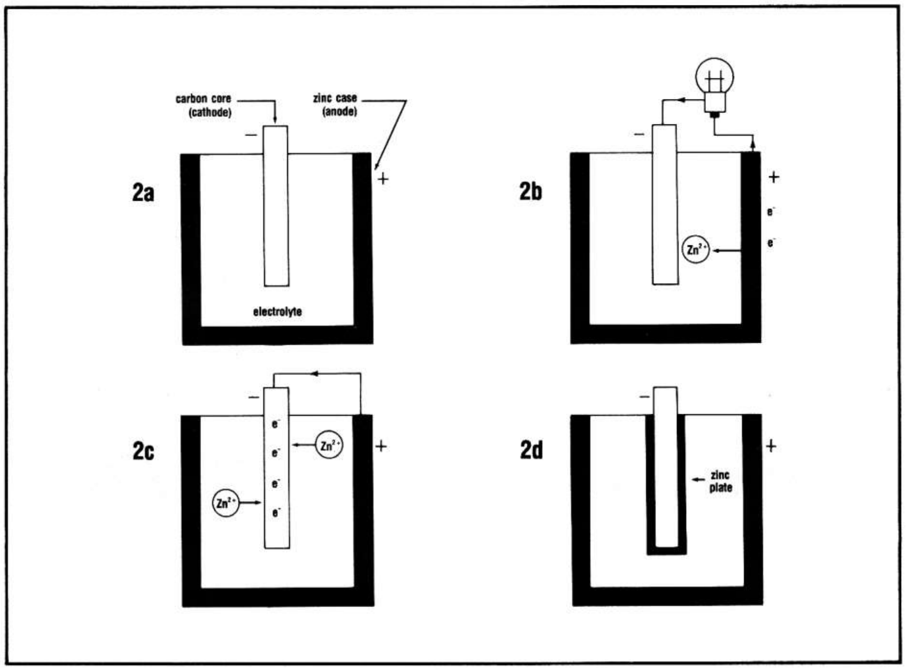

Figure 2: A simple dry cell battery. Electrons are represented by e^- and zinc ions by Zn^{2+}. When electrical contact is made between the anode and cathode, each zinc atom dissolves into a zinc ion and two electrons (Figure 2b). The electrons flow from the anode to the cathode and attract zinc ions to the cathode (Figure 2c). The zinc ions then plate onto the cathode to regain the electrons they lost at the anode (Figure 2d).

George Retseck

Copper Plate

Standard copper electroplating solutions tend to deposit copper at such a rapid rate that the plate is rough and likely to crack and peel. To obtain a smooth coating, copper is electroplated in two steps: first, a copper strike is applied; then an acid copper plate. The copper strike bath consists of a low concentration of copper ions in a cyanide-based electrolyte. This, coupled with low current densities[3] and short plating times, produces a controlled rate of metal deposition. The resulting plate of copper is about five microns thick and adheres well to steel. Now a thicker layer of copper can be plated on without cracking.

Acid copper plating baths consist of a copper sulfate electrolyte which contains a higher concentration of copper atoms than copper strike baths. Higher current densities and longer plating times produce a copper plate about four times thicker than the copper strike. After these steps, nickel or chromium can be plated on.

Nickel Plate

Nickel easily plates onto bare steel or copper-plated steel in a single step using a nickel sulphate solution. The current density is about the same as that used in acid copper plating, but the plating times usually are longer. Very high plate hardnesses can be obtained with nickel depending on how variables such as plating time, electrolyte temperature, and current density are controlled. Nickel plate is hard and durable, but it tarnishes easily and must be polished frequently to maintain brightness. For this reason, chrome is usually plated on top of nickel. When used as an undercoat for chrome plate, nickel plate is usually applied about 30 microns thick.

Chrome Plate

There are two varieties of chrome plating: hard chrome and decorative chrome. Hard chrome plates are very thick (from about 2.5 microns to 500 microns or more), very hard, and corrosion resistant. They have a low coefficient of friction and adhere strongly to the base metal so no metal undercoating is needed. These properties make hard chrome plate a great surface coating to use where sliding wear is a problem. For example, piston rings in automobile engines can last five times longer when hard chrome plated.

Decorative chrome is very similar to hard chrome plate except that it is much thinner (from about 0.13 to 1.3 microns) and, due to a slightly different plating procedure, is not quite as hard. For best results, decorative chrome should be applied over metal undercoating(s). This is the type of chrome plating found on bicycle frames. Decorative chrome plating requires an electrolyte (usually chromic acid) that contains a high concentration of chromium atoms and liquid catalyst to make the plating reaction occur. The anodes, usually made of an insoluble lead alloy, provide the surface upon which chromium atoms are ionized. Current densities are about three times higher than for nickel plating, and plating times are very short.

Table 1 shows cleaning and plating sequences which may be performed on bicycle frames. Please keep in mind that this information doesn't reflect the exact procedures used on bicycle frames. Actual cleaning and plating operations can be much more complicated.[4] For example, the rinses between cleaning and plating can require several steps. Also, there are many plating solutions to choose from, as well as literally hundreds of chemical additives to slow the rate of metal deposition, enhance brightness, and level small surface irregularities. These variables, in addition to current density, plating time, and bath temperature make electroplating more of an art than science.

Incidentally, by altering the chemical conditions of the plating process, it is possible to obtain chrome plate of different colors. The most familiar non-silver chrome plate is black chrome.

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[3] *Current density is the amount of electricity per unit area placed on the cathode to ensure a good deposition of metal ions.*

[4] *For a lengthy discussion of metal cleaning and electroplating procedures, see the* Metals Handbook, *9th edition, volume 5 (The American Society of Metals, 1982).*

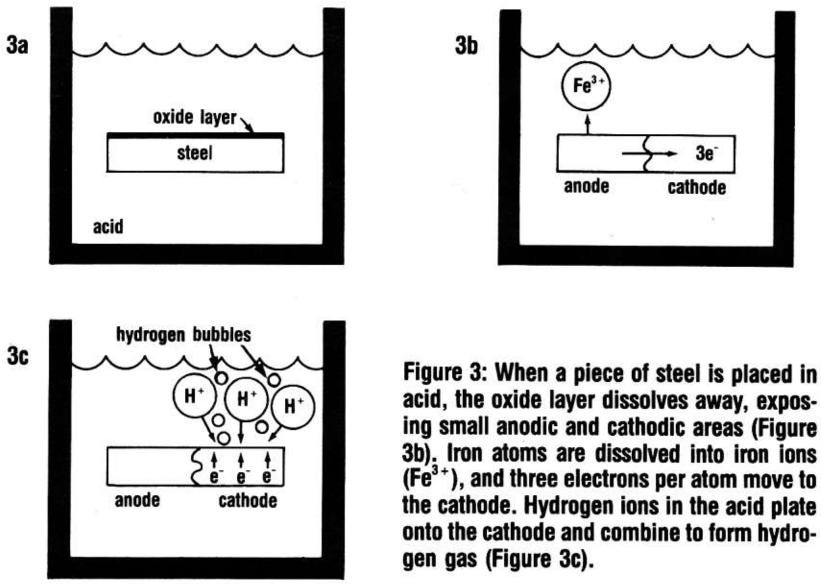

Figure 3: When a piece of steel is placed in acid, the oxide layer dissolves away, exposing small anodic and cathodic areas (Figure 3b). Iron atoms are dissolved into iron ions (Fe^{3+}), and three electrons per atom move to the cathode. Hydrogen ions in the acid plate onto the cathode and combine to form hydrogen gas (Figure 3c).

Table 1 Steps Involved in Chrome Plating (Copper, Nickel, Chrome Plate)

buff
degrease
rinse
pickle
rinse
copper strike
rinse
copper plate
rinse
nickel plate
rinse
chrome plate
rinse
buff (if necessary)

Problems with Electroplating

Unlike painting, electroplating and associated cleaning methods can actually detract from the strength of a frame.[5] Several problems can crop up if the plating process is done carelessly. One of the worst problems occurs at the start of the plating process: cleaning the frame in the acid pickling tank.

Why are acids used to clean frames? Acids contain certain chemical species that aggressively attack and dissolve iron oxides, which is good. But after the oxides are removed, the acid proceeds to corrode the bare steel. This occurs because steel (like all other metals) has microscopic portions of its structure that have a greater tendency to dissolve than others. These anodic areas are bonded to cathodes, so they are in electrical contact. The dilute acid solution used in the pickling process is a great electrolyte; dipping a frame into the pickling tank completes the formation of thousands of electrochemical cells, so corrosive attack begins over the entire surface of the frame.

As the corrosion action begins, iron atoms begin ionizing at the anodes, so there has to be some sort of plating action at the cathodes (see Figure 3). Certain constituents of the acid and the water used to dilute the acid begin plating onto the cathode surface. These constituents combine, with the help of excess electrons at the cathodes, to form gases, water molecules, and different types of ions. The concentration of gas at the cathodes increases with time, and eventually forms gas bubbles. These bubbles rise and new ones begin forming at the cathodes. We'll discuss the significance of this gas a little later.

As the anodic areas continue to corrode, the acid becomes progressively richer in iron and other metal ions and atoms (some alloying elements in the steel are ionized, some aren't). The acid prevents any of these iron or metallic ions from plating onto the cathodic surfaces, so they remain in the electrolyte. It's apparent, then, that the pickling process literally eats away the steel surface, thinning the tubes. The amount of thinning varies considerably depending on the condition of the steel and the strength and exposure of the pickling bath, but losses in wall thickness of up to three percent[6] are not uncommon. And if the pickling solution is allowed to get inside the tube, then wall-thickness reduction could easily be six percent.

Whatever the percent reduction in tube thickness, there will be a corresponding increase in stress on that part of the frame. And as Part I of this series showed, small reductions in wall thickness become increasingly significant as the thickness of the tube decreases. So it's important to minimize reductions in wall thickness to acceptable values (probably fractions of one percent) by cleaning the frame prior to pickling so the frame spends minimum time in the pickling tank, and making sure that the insides of the tubes aren't pickled. A sure sign that a frame stayed too long in the pickling tank is a roughened surface on it caused by preferential corrosion (i.e., some areas are more anodic than others).

A related problem is *pitting*. Pitting usually occurs during *electrolytic pickling*. In this process an electrical current is passed through the component (or anode) to accelerate pickling. When small pieces of oxide break off, exposing bare metal to the acid, the metal dissolves at a rate faster than normal and a pit is produced.

Hydrogen Embrittlement

As I said earlier, one of the reactions that takes place at the cathode during pickling is the formation of gases. Usually, hydrogen is the gas evolved at these sites. Single hydrogen atoms[7] are very small and can easily be absorbed by steels. If enough hydrogen is absorbed, the steel can suffer a drop in mechanical properties[8] because the steel becomes embrittled.

Nobody knows exactly how hydrogen embrittles steel, but here are two theories. Since hydrogen is such a small atom, one theory says that it can take up positions between iron atoms; the iron atoms become bonded to hydrogen atoms instead of neighboring iron atoms (see Figure 4). The bond strength between iron and hydrogen atoms is assumed to be less than that between just iron atoms, so cracks can form more easily in the steel at low stresses.

The actual strength of metals (and most other crystals) is only a fraction of what it theoretically should be. This phenomenon puzzled metallurgists for a long time until it was theorized (and later proved) that atom-sized defects are present in crystals (these defects make metals malleable). Hydrogen atoms absorbed by steel diffuse and eventually come to rest at places where they fit in well; a second theory suggests that they collect at crystal defects (see Figure 5). Hydrogen atoms residing at these defects combine to form hydrogen gas. This gas can't move around as easily as single atoms can, so a pressure is exerted on the surrounding iron atoms. This local pressure pries the steel apart, so only small external stresses are needed to form cracks. Whatever the actual mechanism, hydrogen embrittlement begins in the pickling tank.

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[5] *Paint itself is harmless, but some chemicals and procedures used to prepare and clean steel for painting, like phosphating, baking, and chemical stripping can, in theory, affect the strength of frames.*

[6] *Reference 4, p. 13.*

[7] *This is in contrast to hydrogen gas, which has two hydrogen atoms bonded together.*

[8] *Mechanical properties include tensile strength, yield strength and ductility.*

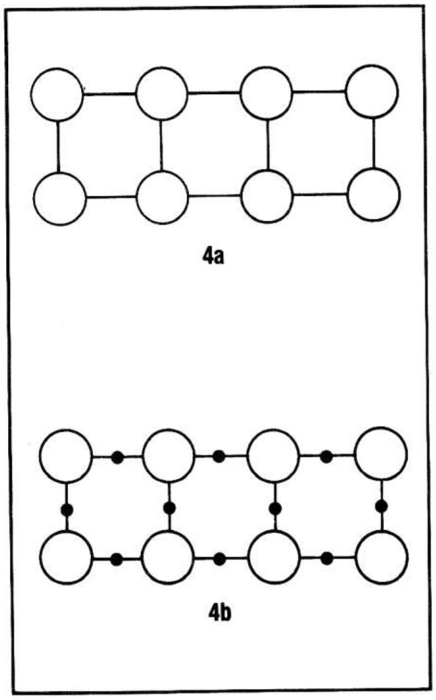

Figure 4: Iron atoms in steel. When hydrogen enters steel, they may take up positions between the iron atoms as depicted by the dark circles in Figure 4b. The bond strength between iron atoms will be reduced, increasing the likelihood that low level stresses will crack the steel.

George Retseck

The threat of hydrogen embrittlement is also present during electroplating. If the plating process is less than 100 percent efficient (i.e., all the electrical energy does not go into plating metal ions onto the cathode), some fraction of electrical energy is used to create unwanted chemical species, like hydrogen. Chrome plating has a very low plating efficiency (about 20 percent; this is why the current density is so high in chrome plating), so a lot of hydrogen will be produced. Copper and nickel can be electroplated with much higher efficiencies, but small amounts of hydrogen will still be formed. Hydrogen formed during electroplating can then diffuse either directly into the base metal, or through the undercoatings to the base metal. And if pickling and electroplating solutions enter tubes, hydrogen will be formed on two surfaces instead of one. It is these multiple exposures to hydrogen (similar to multiple particle blastings) which can compromise the mechanical properties of steel tubing.

The presence of hydrogen bubbles at the cathode can also compromise the aesthetics of chrome plate. These bubbles prevent the chromium ions from plating smoothly and securely onto the cathode. This results in small pits in the plate which can be removed only by stripping the old plate and starting over. To avoid this, wetting agents are added to the electrolyte to promote detachment of bubbles from the cathode.

Corrective Measures

The entire electroplating process, from acid pickling to chrome plating, takes approximately one hour. In this time span, a great deal of hydrogen can be absorbed. The steels most susceptible to hydrogen embrittlement have yield strengths of about 200,000 psi or more. Since the steels used to make bicycle frames have yield strengths of about 100,000 psi or less, hydrogen embrittlement should be less of a problem. However, the amount of time a component is exposed to hydrogen isn't the only factor in determining how much hydrogen is absorbed; surface finish, microstructure, and residual stresses caused by brazing also play a role.

Tests have shown that the more crystal defects in the steel there are, the more hydrogen is absorbed. So there appears to be a relationship between the two, even though this mechanism of embrittlement stated earlier is conjecture. Frames that have been particle blasted prior to plating are likely to pick up more hydrogen than those that weren't because sandblasted steel exhibits more crystal defects.

Similarly, hydrogen may tend to segregate to areas of the frame that have been distorted by brazing. So it's possible that frames can absorb too much hydrogen, especially since thin tubes are more quickly saturated with hydrogen than thick tubes. If it can be determined that frame tubes absorbed a lot of hydrogen (an analysis that can be done, but that is extremely expensive), corrective measures can be taken.

A low temperature heat treatment will reduce hydrogen's embrittling effect. Low temperature baking is sufficient to remobilize hydrogen atoms, which can then diffuse out of the steel. Since temperatures are low, the structure of the steel isn't changed appreciably from its original (before plating) properties. Although there are no established standards for heat treating hydrogen-embrittled bicycle frames, baking in the range of 200° C – 240° C (390° F – 465° F) for three to four hours is suitable.[9] Electroplaters I've talked to who plate bicycle frames are aware of hydrogen embrittlement but don't perceive it as a problem. As a result, they don't bake the frames after plating.

Stripping

If a poor job was done electroplating copper, nickel, or chrome, the plate can be stripped off by immersing the plated areas in acid. And like pickling, stripping can be done electrolytically to save time. But acids must again be used; their concentration and type vary, depending on the metal which must be removed. Suppose, for example, a frame were nickel plated. Concentrated nitric acid can be used to strip it, but this will also attack the steel tubes. If chrome must be removed, the metal undercoat may be attacked. The frame may then have to be treated with yet another acid to prepare it for new chrome plating.

Redoing a bad plating job or refinishing a frame can result in further reductions of wall thickness if the plate closest to the steel is removed, and/or if stripping acids enter the tubes. In addition, more hydrogen can be picked up by the steel during stripping and subsequent recleaning and replating. This might lead to dangerously high levels of hydrogen in the steel.

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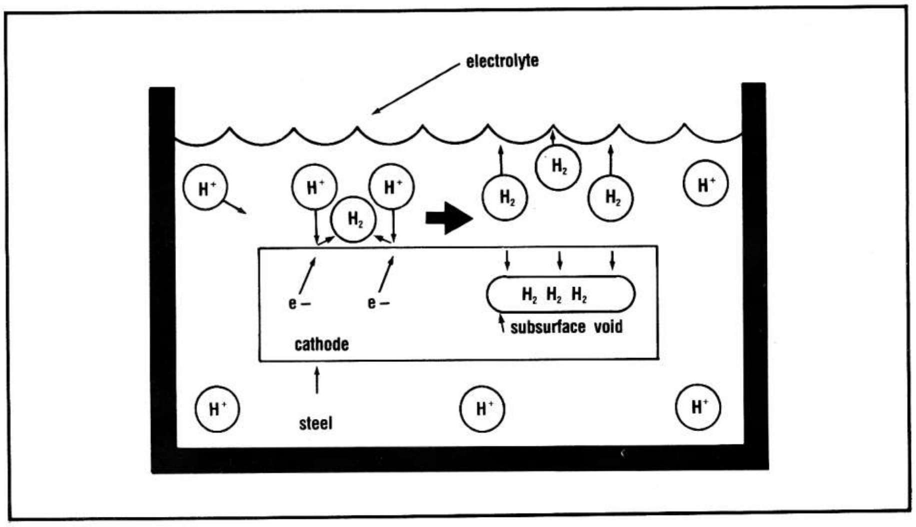
[9] *Reference 4, p. 81.*

Figure 5: Hydrogen ions in the electrolyte pick up electrons at the cathode and form hydrogen atoms. These atoms can either combine to form a gas bubble on the surface of the cathode, or diffuse into the steel.



Corrosion

Some framebuilders go to great pains to make sure that pickling and plating acids don't enter the tubes. If chainstays are being chromed, they ask the electroplater not to immerse the bottom bracket area. When forks are plated, air holes are brazed shut. But if the entire frame is chrome plated, or if the framebuilder doesn't explicitly instruct the electroplater, it's likely that pickling and plating acids will enter the tubes. Once these acids are in the tubes they're difficult to get out. Rinses between pickling and plating must be done carefully to ensure that the insides are thoroughly cleaned. The problem here is that the rinses may not get inside the tubes as far as the electrolyte did because thin tubes are hard to flush out unless there are bleed holes. Any acid residues left inside the tubes eventually dry out and leave behind small crystals of acid salts.

If water then enters the tubes (either as rain or humid air), the acid salts left in the tubes will redissolve to form a new liquid or paste electrolyte. The concentration of this acid will be higher than that used in electroplating because the ratio of acid salt to water is higher. The stage is set for tubes to corrode from the inside out. This can be a particularly dangerous situation since it's not apparent when areas of a tube have thinned to unsafe dimensions. Figure 6 shows what can happen to the inside of a chrome plated tube.

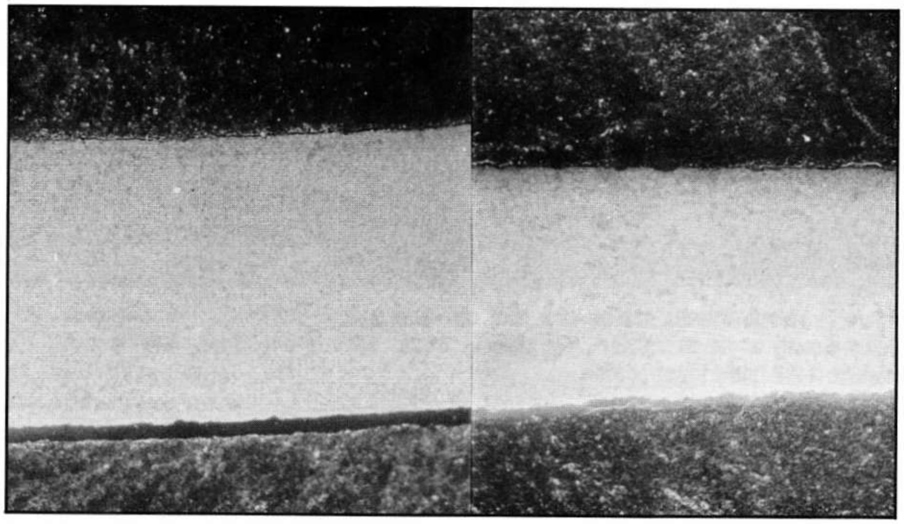


Figure 6: These photos were taken from two locations inside the head tube/down tube joint of a high-quality frame several years old. They are cropped together to show the differences in tubing thickness at each location. Plating solutions entered the tubes when the lug was chromed and were not completely flushed out. As a result, severe corrosion occurred, causing an estimated 20 percent difference in wall thickness between the two locations pictured. 40 times magnification.

Microcracks

Chromium is a more reactive metal than iron, but exposure to oxygen in air forms a very thin but tough oxide layer on its surface, which protects the remainder of the chrome from corroding. However, you may have noticed chrome plating that appears to be rusting. This isn't because the chrome layer has corroded. Rather, moisture has passed through the chrome plate and has rusted the steel beneath.

Chrome plate can have a porous or *microcracked* structure during application depending on the plating process used. The reason why the plate becomes cracked during application isn't known. Perhaps it is due to the way the plate grows, or maybe the crystal structure of the chrome changes during plating, causing it to contract. Perhaps plating cracks in an effort to relieve its surface tensile stresses. Cracks in thick plates are usually restricted to the surface because cracks that form closer to the substrate are filled by plating on top. But thin, decorative plating is usually cracked all the way through and it allows oxygen and water to reach the base metal, causing it to corrode.

This is one reason why metal undercoatings are used. But the choice of undercoatings is not accidental. Nickel is used because it is anodic to chromium and thus corrodes instead of the chrome. Since iron is anodic to nickel, corrosion that makes it past the nickel plate means the steel will corrode. Corrosion that has reached the steel causes the chrome to blister. Copper plate beneath nickel helps improve nickel's corrosion resistance and thus protects the steel better.

For maximum corrosion resistance then, steel frames should be copper, nickel, then chrome plated. However, bicycle frames are frequently only nickel and chrome plated or just chromed with no undercoats at all. This eliminates the two-step copper plating process, perhaps to save money, or maybe because manufacturers and builders feel that frames don't need the extra corrosion protection. Just chrome plate may be acceptable, as long as the plate is thick and isn't cracked all the way through. Figure 7 shows a thick, crack-free plate with no undercoat.

Fatigue

Fatigue is a process whereby metals fail due to repeated application of stresses. Sometimes the stresses are well below the yield strength of the metal, but stresses near surface or structural discontinuities can be very high. This may produce a crack which can grow and cause eventual failure. Bicycle frames, as noted in other *Bike Tech* articles,[10] are subjected to repeated stresses, so nothing should be done to frames to decrease their fatigue resistance.

However, it's been shown that chrome plated surfaces decrease the fatigue strength of steel.[11] This happens because the plating contains residual tensile stresses which stretch the surface of the base metal. When this happens, the base metal develops its own surface tensile stresses, so chrome plating can have the opposite effect of peening by locking in rather than relieving these stresses. As stated earlier, these residual stresses may work themselves out by cracking the chrome plate.

In addition, cracks in the chrome plate can act as stress raisers which may grow into the base metal. However, fatigue tests that I'm aware of have not utilized samples with copper and/or nickel undercoatings,[12] so test results can be applied only to those frames with no undercoatings, such as in Figure 7.

Summing Up

The most important concern in the plating process is to keep the pickling and plating acids from getting inside the frame tubes. If those acids get in, the tubing will be thinned twice as much, hydrogen will be absorbed on both surfaces, and, unless these harsh chemicals are completely rinsed out, they can lead to severe corrosion problems later on. These problems can be avoided if only the front fork or the chainstays are chromed — the air holes can be brazed shut and it's not too difficult to keep the bottom bracket shell out of the pickling and plating tanks. But if the entire frame is chrome plated, it is

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[10] *See "Can Surface Finish Affect the Strength of Your Frame? Particle Blasting, Part II,"* Bike Tech, *February 1984, and "What Is Fatigue?"* Bike Tech, *October 1982.*

[11] Modern Electroplating, *F. Lowenstein, Ed. (New York: John Wiley and Sons, Inc.) p. 128.*

[12] *Reference 11, p. 128.*

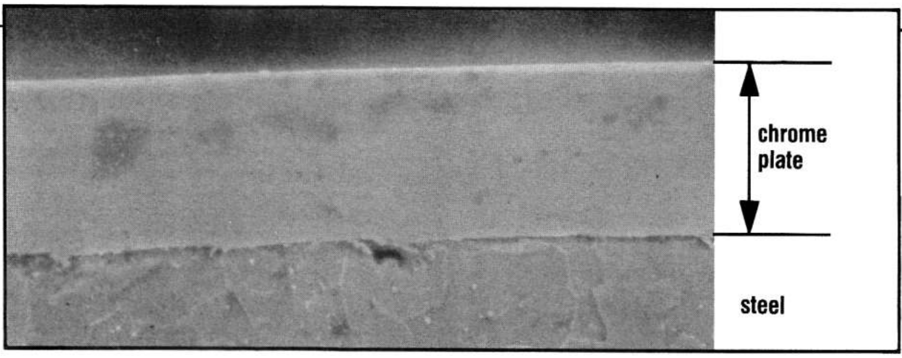

Figure 7: This is a cross section of a seat stay from a Japanese frame. The chrome is plated directly on top of the steel. The plate is about 16 microns thick, and is not cracked. 1435 times magnification.

inevitable that these acids will seep in unless special care is taken to seal the head tube, seat tube, bottom bracket, and all the brazing air holes.

It may seem excessive to bother plating copper and/or nickel on frames if a crack-free chrome plate can be put on. This may have been the reason why the frame in Figure 7 was not undercoated. However, a slapping chain can put nicks in the thin chrome plate on the chainstay and expose the steel below. The same is true if chrome is worn off the dropouts. Thus it would be worthwhile to have a thick, hard nickel plate beneath the chrome to help resist wear and corrosion.

If frames are chrome plated with no undercoating, their fatigue resistance will be lowered. But is this drop in fatigue strength enough to cause concern? Maybe, maybe not; but to be on the safe side, I don't recommend chroming high stress areas of the frame like the front fork. I also suggest for better fatigue resistance and corrosion protection that chrome be done on top of a copper and nickel undercoat. The chrome plating on the frame in Figure 7 may not be indicative of all bicycle chrome work, but I suspect that it is common practice, especially in Europe, to plate only with chrome.

Interestingly, the latest (1984) Columbus tubing catalogue lists some guidelines for chrome plating and pickling their tubing. This is the first time, to my knowledge, that any of the bicycle tubing manufacturers has offered any such information. Columbus does "not recommend" that their tubes be chrome plated. They also recommend that their tubes be pickled in a mild three to four percent solution of sulfuric acid at a temperature of 40° C (104° F). This is a much less aggressive solution than that recommended by other sources.[13] These recommendations indicate to me that Columbus is concerned about the dangers of thinning and pitting their tubing in a strong pickling bath.

Columbus doesn't indicate whether chrome plating voids the warranty on their tubing, but you can be sure that they'll not warrant any tube that fails from the effects of pickling and/or plating. Thus it is important to be aware of the problems inherent in the electroplating process so that the already thin tubing used in bicycle frames will not be thinned, corroded, or embrittled with hydrogen any more than the process requires.

Acknowledgement

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Postscript

Steel tubing undergoes a reduction in wall thickness at each step of the frame building process. The high temperatures of brazing cause oxidation of the tube's surface. Particle blasting and pickling both take their toll on tubing wall thickness. Chrome plating can create surface tensile stresses and, if the plating bath electrolyte gets inside tubes and isn't thoroughly rinsed out, the residual acids will certainly cause the tube to rust on the inside.

Any additional particle blasting or pickling of the frame, to remove a defective finish or as the first step in refinishing, removes still more metal. All three procedures, even when done with great skill, will reduce tubing wall thickness, leave residual stresses and corrosive acids in the tubing, pit the tubes, and/or embrittle the tubes with hydrogen.

I believe the major question that has arisen from this series of three articles on the effects of surface finish on frames is whether or not frame tubing was ever designed to be subjected to particle blasting, pickling, and chrome plating. Most frame tubing is quite thin to begin with; how much thinner can it get before its structural integrity is compromised? And when do the stress raisers put into tubing become too large or too numerous?

Most frame tubes appear thick enough to withstand some abuse they might not have been designed to take. This is fortunate because particle blasting, pickling, and chrome plating are cost-effective, time-saving, and aesthetically pleasing steps in frame building that few builders can do without. I would caution against the use of these procedures when working with ultra-thin tubing like Reynolds 753 and Columbus Record and KL, but even then, if these procedures are done properly, few problems should arise. But disregard or ignorance of the potentially damaging effects of particle blasting, pickling, and chrome plating could set a frame up for early and possibly dangerous failure.

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[13] *Reference 4, p. 69.*