GalvInfoNote	Protecting Galvanized Steel Sheet Products from Storage Stain
3.2	REV 3.0 OCT 2020

Introduction

Storage stain, when related to galvanized sheet products, is a corrosion stain that is typically white, but which can also take the form of a grey or black deposit on the surface. Since the most common form of discoloration is white in appearance, storage stain is often called **white rust**. It can occur when sheets of galvanized steel that are in close contact (in a coil or stacked in lifts/bundles) get wet, either by direct water intrusion, or condensation between the surfaces. The discoloration is due to the corrosion products that form after zinc reacts with moisture in the absence of free air circulation.

Building erected using roll-formed galvanized panels from a bundle that had extensive amounts of white rust.

Note: This voluminous amount of white rust did not occur after erection of the building siding. When freely exposed to air, the products of zinc corrosion form a thin, tenacious film. The surface accumulation seen here occurred while the sheets were stored in a wet bundle.

Before discussing the issue of storage stain in more detail, let's first review what happens when a galvanized (zinc) coating corrodes in the environment.

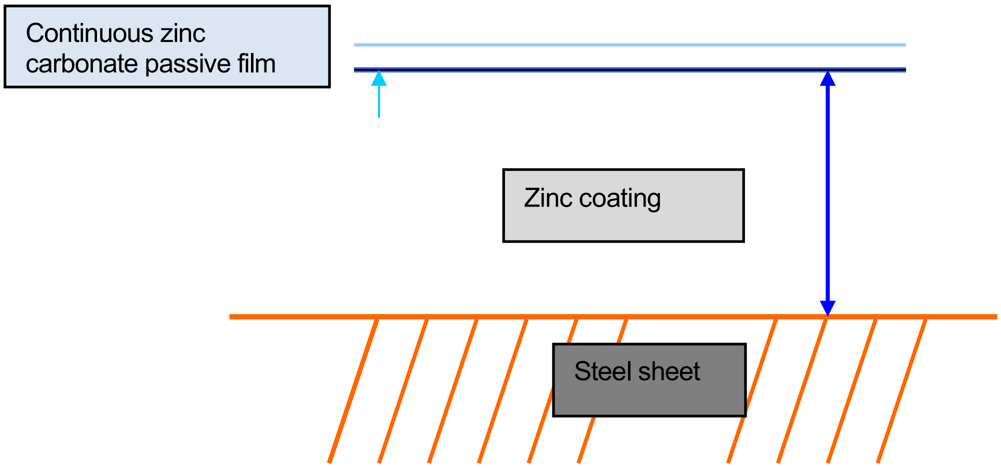
Why Does Zinc Protect Steel?

Zinc, by its very nature, is a "reactive" metal and tends to corrode quite readily when exposed to moisture. Why then does it protect steel when a zinc-coated sheet is exposed to the atmosphere?

When zinc corrodes in the presence of air and moisture it undergoes a series of chemical reactions, changing from metallic zinc on the surface to other chemical compounds. In air, newly exposed zinc reacts with oxygen to form a very thin oxide layer. In the presence of moisture the zinc oxide reacts with the water, resulting in the formation of zinc hydroxide. Over time, and under the influence of cyclic weathering, the final corrosion product is zinc carbonate (formed by the reaction between zinc hydroxide and carbon dioxide in the air). Zinc carbonate is a thin, tenacious, compact, and stable (insoluble in water) film. When the surface is further exposed to rain or condensation, the protective film serves as a barrier between the moisture and the zinc underneath. This type of chemical layer is called a **passive film**. It is the presence of this passive film that slows down the reactivity of the zinc, thereby dramatically reducing the corrosion rate of the zinc coating.

The series of chemical reactions described above are:

$$Zn + \frac{1}{2}O_2 \rightarrow ZnO$$
$$ZnO + H_2O \rightarrow Zn(OH)_2$$
$$Zn(OH)_2 + CO_2 \rightarrow ZnCO_3 + H_2O$$



A through-thickness schematic that shows the continuous, protective oxide/carbonate passive film that forms on galvanized sheets exposed to the atmosphere.

Typically, when low carbon steel corrodes, the corrosion products (iron oxide and/or iron hydroxide) do not form a continuous, protective, passive film. Instead, they tend to spall or develop cracks, which allows moisture and air access to the iron, continuing the corrosion reaction. **The difference in oxide film-forming behaviour between iron and zinc is the underlying reason for galvanizing extending the life of steel.** For more information on how zinc protects steel, see GalvInfoNote 3.1.

In most applications, the passive surface film that forms on zinc, while tenacious, is not totally protective, and continued corrosion does occur over time. However, because of the nature of the passive film, the corrosion rate of a zinc coating is diminished substantially – anywhere from 10 to 100 slower than bare steel.

Why is Zinc Susceptible to Storage Stain (White Rust)?

As stated above, zinc is very reactive metal. It exhibits a low corrosion rate only because a continuous passive film forms on the surface. A key part of the corrosion mechanism is that, after wetting, the surface needs to dry in air in order to develop and maintain this passive layer. It is during the drying part of a rain cycle that the zinc carbonate passive film develops. Atmospheric wet-dry cycles are necessary for zinc to develop passivity.

When galvanized sheet gets wet while still in coil form, or stacked into bundles at a roll-forming plant or jobsite, storage stain can result. Storage stain (usually white rust) is simply the chemical compound, *zinc hydroxide (ZnOH)*, which forms when zinc is in contact with moisture. It does not convert to a zinc carbonate passive film because the tightly packed sheets are not freely exposed to oxygen/carbon dioxide-containing air. A protective zinc carbonate film never gets a chance to form. Since the corrosion reaction continues to proceed as long as the surfaces are wet and starved for oxygen and carbon dioxide, a large accumulation of zinc hydroxide can form. Zinc is a very reactive metal in the presence of moisture when conditions do not allow the passive film to form.

When white rust does occur, there is an actual loss of zinc coating, and some of the zinc that is intended to protect the coated steel product while in service is consumed by oxidation. The extent of the damage is primarily dependent on:

1. The exposure time to moisture,

2. The temperature that is experienced during storage, and
3. The presence of accelerating corrosive agents, such as chloride-containing salts.

Often, the amount of white rust appears to be quite heavy when, in fact, the amount of corroded zinc is small. This occurs because ZnOH is somewhat flocculent, and builds up in the area of the wetness. When ZnOH dries in the open air it converts to zinc oxide (ZnO). If the application is not aesthetically critical, the galvanized coating should perform very well and meet the requirements and expectations of the end user. In most instances involving outdoor exposure, the white rust will disappear over time, as it is either washed off by rainfall or is converted to zinc oxide and then zinc carbonate.

The surface of the zinc coating in the area that experienced white rust is "etched" and no longer has the bright, reflective appearance of as-produced galvanized sheet. Removing the white rust (see section at the end of this article) will not eliminate the etched appearance. This is why, for applications where appearance is critical, galvanized sheet with white rust may not be acceptable.

There are times, albeit seldom, when the sheets have been wet for a long time; long enough that the corrosion of the zinc coating is severe. In these cases, the product may no longer provide the corrosion resistance desired for the application. In addition, the storage stain may take on a dark grey or black appearance. When the stains on galvanize turn black it usually means that iron has become part of the corrosion product, i.e., enough zinc has been consumed that iron from the steel substrate is involved. Nevertheless, it takes a trained observer to determine whether or not the amount of corrosion that has occurred is severe or not.

Why does some galvanized sheet products show initial dark, not white, staining?

It has been observed that initial, relatively light, storage stain on some water-damaged galvanized sheet surfaces is not white, but dark grey to black. This has been seen to be the case with product that has been temper rolled (skin passed).

The process of skin passing involves light cold rolling of the sheet with steel rolls to impart an even, smooth, matte surface finish. The peaks on the surface of the work rolls are pressed into the surface of the zinc coating during skin-passing, creating depressions (depth between 30-70 μin [0.75-1.75 μm). Depending on the rolling force, the "hit" by the rolls covers up to 50% of the original surface.

A recent study[1] found that the velocity of Al-based oxide segregation on the surface of temper-rolled HDG was much higher than that on HDG without temper rolling. This was attributed to the surface areas affected by the temper rolls having much more Al-based oxides present due to the Zn crystal grains in the coating being refined by the slight cold reduction, creating an increased number of grain boundaries that can serve as Al diffusion paths. Even unrecrystallized grains could increase the number of formation sites for Al-based oxides as they contain numerous dislocation sites from temper rolling that that can serve as Al diffusion paths. It has long been known that non-temper rolled galvanized sheet has Al-based oxides present on the surface. This study found that on freshly coated galvanize this level was 2 mg/m^2, rising to a stable level of about 3 mg/m^2 after 12 weeks aging at 20˚C. The Al oxides were found primarily at the grain boundaries of the zinc. For the temper rolled material, the Al-based oxides measured at about 7 mg/m^2 after the same aging time, were still on an upward trend, and were also present at locations away from the grain boundaries. The driving force for the diffusion of the Al is, that below 150˚C, the 0.2% Al (present in all zinc used for continuous galvanizing) is supersaturated in the coating just after galvanizing. Temper rolling promotes much faster precipitation of the supersaturated Al phase to the surface.

The above findings may help explain the reason for the dark appearance of storage stain on temper rolled galvanize. It has been observed that the storage stain on 55% Al-Zn alloy-coated sheet (Galvalume™) is seen as black corrosion products when water-damaged. Mild to moderate storage stain damage to Al surfaces is generally black in appearance (Al oxide), whereas it is white on Zn surfaces (Zn oxide). Galvalume coatings are largely composed of Al, whereas galvanize is largely zinc. The migration of Al to the surface of skin passed galvanized sheet to a level of at least twice that of non-temper rolled galvanize, could well be the reason for storage stain on the former product appearing dark.

While there have been no published studies specific to the nature of storage stain on skin passed galvanize versus non-skin passed, a study[2] on steel surface defects reported that "the manner in which light reflects off the surface depends not only on the surface roughness but the nature of the material." This mechanism is often the reason *that some oxides "can appear white whereas others appear dark, even though they of similar chemistry." This phenomenon is also seen on zinc surfaces damaged by fretting corrosion, where black surface marks are seen to be composed entirely of zinc oxide (see GalvInfoNote 3.5).*

Preventing Storage Stain

Clearly, it is very desirable to take every precaution to avoid storage stain on galvanized sheet. Often, the customer's application requires the aesthetic appearance of a bright, galvanized surface, and no amount of storage stain is acceptable. Fortunately, practices have been developed to delay the early formation of storage stain on galvanized sheets.

Chemical Treatments (Passivation)

The best way of minimizing the chance of white rust forming during shipment and storage of coils, lifts of sheared blanks, or bundles of roll-formed panels, is the application on the galvanizing line of a very thin and invisible chemical treatment by the coated sheet manufacturer. The most common type of passivation treatment has been a water-based chromate coating. Chromate treatments contain hexavalent chromium. They are typically applied by spraying the solution onto the surface, after which the excess is "squeeged" off using rubber-coated rolls. Following this, the passivating film is dried thoroughly before recoiling the coated sheet at the exit end of the galvanizing line.

Due to health, safety, and environmental concerns, the use of hexavalent treatments is being discontinued. They are being replaced by treatments that are free of hexavalent chromium, either those where the chrome is only in the trivalent state, or products entirely free of chrome. Refer to GalvInfoNote 2.10 for more information on these new treatments.

Passivation coatings have been in use for many years, and their performance has been exceptional with respect to minimizing the tendency for staining when the sheets get wet in coil or bundle form. Steel sheet manufacturers use the term "passivation treatment" or "chemical treatment" for this surface treatment. Both terms are used interchangeably. **When an order is placed, it is necessary to specify whether chemical treatment "is" or "is not" required.**

It is important to remember that mill-applied passivation treatments **minimize** the tendency for storage stain; they **do not eliminate** its occurrence if the product is subjected to very adverse conditions. An example would be having a coil get wet during transit to a customer, and then allowing the coil to sit in a warehouse for a long period without any attempt to dry it. Even if the product is ordered with a chemical treatment, it is still important to keep moisture from between the wraps while in coil form, as stacked blanked sheets, or in bundles.

Surface passivation treatments also assist the product in another way. When coated sheets are put into service and exposed to atmospheric environments, passivation treatments help to maintain the bright, shiny appearance. Eventually the brightness diminishes, but the passivation treatment aids in keeping the shiny, metallic appearance for a considerable time. The longevity of this effect depends on the type of treatment, the environment and the relative corrosivity of each location. Also, as the surface dulls, it tends to do so in a more uniform fashion than if the sheets were unpassivated.

Visually, it is generally not possible to tell if galvanized sheet has been passivated. ASTM *Standard Practice D6492 – Detection of Hexavalent Chromium on Zinc and Zinc/Aluminum-Alloy Coated Sheet*, can be used to determine if the sheet has been treated with a chromium based passivating solution. As any hexavalent chrome in the treatment eventually oxidizes to trivalent chrome, this test only works on freshly (at most a few months) passivated sheet.

Another quick method of finding out if galvanized sheet has been passivated, with chrome or non-chrome treatments, is to use a simple condensing humidity test. Place a 4" [100 mm] square of the galvanize sheet as a lid on a beaker containing 140°F [60°C] water and leave for 15 minutes. If the underside remains shiny it is passivated. If it is stained to any degree it is not passivated.

For more information on passivation see GalvInfoNote 2.10.

Passivating Oils

Besides the use of chemical passivation treatments, other surface treatments can be used. The most common are rust-inhibitive oils. These are oils containing corrosion inhibitors that provide some protection from storage stain. The inhibitors are usually polar products designed to strongly adsorb onto metal surfaces. The oil serves as the carrier solution for the inhibitor. As with chromate treatments, the oil is applied by the steel sheet manufacturer on the galvanizing line. A common method of applying the oil is by an electrostatic applicator. These oils are not intended to provide sufficient lubrication for applications such as deep drawing, but they do provide some lubrication and can assist with some forming operations. Another type of oil is “vanishing oil”. It is a volatile compound that evaporates when exposed to air, and leaves behind a corrosion inhibitor on the sheet surface.

Oils are effective in providing protection from humidity rust due to their ability to help prevent humid air from staining the surface between the laps of a coil or sheets of a bundle. They are not so effective, however, in preventing damage from the penetration of bulk water, e.g., rain, between laps.

What Treatment to Apply

Often, the end use defines whether a passivation treatment or rust-inhibitive oil should be applied. Typically, when the end use is one that does not involve painting, the passivation method is best, although some passivates are compatible with painting. If the application requires painting in the manufacturer’s plant, rust-inhibitive oil is usually best, but check with the producer to see if they use a passivate that is paintable.

Because of the changing situation with passivation treatments, it is best for a user to discuss their needs with the galvanized sheet producer. For instance, it is possible to order a product with both chemical treatment and oil. Typically, this combination provides better white-rust protection than either chemical treatment or oil used separately, and should be considered when harsh storage conditions are expected.

When the end use involves spot welding, or coil prepainting, it may be necessary to order the product as unpassivated. When this is the case, **there must be absolute certainty that it will not get wet before it is used.** Precautions that can be taken are explained below.

Additional Ways to Protect Galvanize from White Rust

Besides the use of oils or chemical treatments, there are other ways to minimize the chances of storage stain occurring. A common method involves “wrapping the coil” by the sheet manufacturer. Both plastic and paper wrapping materials are available. The packaging material may have a corrosion inhibitor impregnated into it to provide even better protection.

In addition, the prevention of storage stain is strongly influenced by the methods and practices used for shipment from the steel manufacturer to the customer. It is vital to prevent water intrusion and to use practices that minimize the tendency for condensation during transit and storage. It is especially important to maintain controlled temperature storage (sometimes even during transit), to prevent condensation that can occur if the air temperature drops below the dew point, or if cold steel coils/bundles are moved into a warm, moist environment. See Best Practices below for more information on storing galvanized coils.

How Do Coils Get Wet?

Coils or bundled sheets get wet in two ways:

1. Water from rainfall gets between the sheets while the product is in transit or while it is sitting at a jobsite
2. Condensation.

Condensation occurs when the coil or stacked sheets are below the dew point of the local atmosphere. One way for this to occur is when coils are shipped in cool or cold weather, and then placed into a warehouse that is warmer than the galvanized steel itself, and where the humidity is not at a controlled low level. Under these conditions, moisture can condense onto the surface of the steel as the cold coil causes the nearby air temperature to drop below the dew point. This is similar to the condensation of moisture onto a cold windowpane.

Condensation can occur in other ways that are not as obvious as that above. For example, even if the coil temperature and the temperature inside the local warehouse are about the same when the coil arrives, and the warehouse is not temperature controlled, the influx of warmer, moister air after a period of cold or cool weather, might allow condensation to occur on coils and even form between adjacent wraps. Surface tension also draws any moisture on the coil wall further into its interior. Once moisture gets between laps, it will not evaporate because air movement is absent. If this happens, even the best chemical treatment cannot protect against storage stain for longer than about six weeks.

See the next section on Best Practices to assist in avoiding condensation during warehouse storage.

Because there is no absolute way to totally prevent storage stain once the material gets wet, it is important for the best practices to be applied at all steps in the process.

Always keep in mind – if galvanize is kept dry, storage stain will never be an issue.

Best Practices

1. The steel manufacturer needs to apply the chemical treatment and/or oil in a controlled manner to cover the entire surface area of the sheet.
2. If possible, the coils should be wrapped with paper that is specially made for this application.
3. **The shipper needs to protect the steel during shipment to the customer's plant. Even if the coils/bundles are wrapped, ship only in covered, watertight conveyances. If it is necessary to use an uncovered conveyance, wrap the load completely with a tarp to assure no water intrusion if it rains during shipment. Avoid tearing the wrapping paper.**
4. The customer should store the coils in a climate-controlled warehouse. Use the material promptly. Whenever possible, try to avoid storing the product for extended periods of time (in excess of two months).

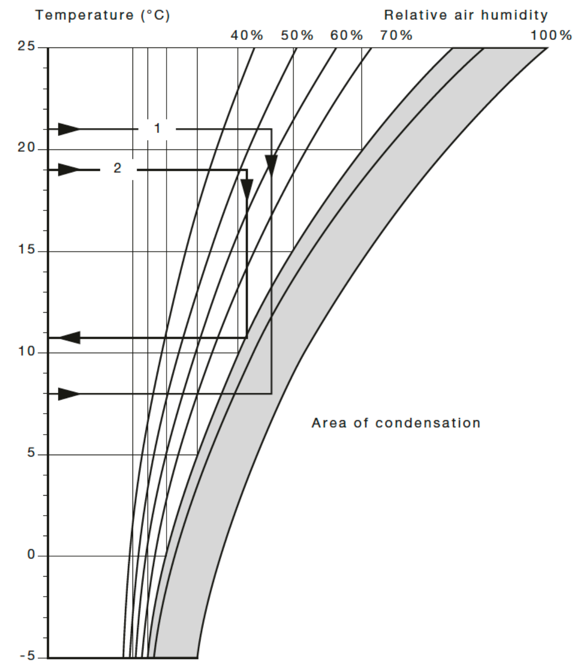
The two charts below can be used to help avoid the danger of condensation occurring on steel coils during storage. By knowing the temperature and relative humidity in a warehouse, the lowest steel temperature at which it is safe to store coils can be determined. Condensation can occur in climate-controlled warehouses in the cooler months after long shipping transit times, or even on coils that are near shipping doors that are left open. In warehouses without climate control, a sudden weather change from cool to warm and humid can cause condensation on the steel.

To avoid condensation issues on steel that is known to be cold after transit in low temperature conditions, the material should be allowed to acclimatize itself, i.e., put into temporary locations where the steel temperature is above the local dew point, until it warms enough to be stored in the warehouse. If the steel coils or bundles are wrapped with paper, the best practice is to not remove the wrapping until the steel temperature is above the dew point. The charts below will be very useful in determining when this is the case.

Diagram used to determine danger of white rust caused by condensation

Example 1: Strip temperature of 8 °C, room temperature of 21 °C, relative humidity of 55% → danger of white rust.

Example 2: Storage area of 19 °C, relative humidity of 50% → minimum strip temperature of 11 °C required.



Source: Hot-dip galvanized steel strip, Technical Terms of Delivery, voestalpine Stahl GmbH, 2011, p. 48

Air Temperature in Degrees Fahrenheit

Air Temp °F	**% Relative Humidity**																		
	100	**95**	**90**	**85**	**80**	**75**	**70**	**65**	**60**	**55**	**50**	**45**	**40**	**35**	**30**	**25**	**20**	**15**	**10**
110	110	108	106	104	102	100	98	95	93	90	87	84	80	76	72	65	60	51	41
105	105	103	101	99	97	95	93	91	88	85	83	80	76	72	67	62	55	47	37
100	100	99	97	95	93	91	89	86	84	81	78	75	71	67	63	58	52	44	32
95	95	93	92	90	88	86	84	81	79	76	73	70	67	63	59	54	48	40	32
90	90	88	87	85	83	81	79	76	74	71	68	65	62	59	54	49	43	36	32
85	85	83	81	80	78	76	74	72	69	67	64	61	58	54	50	45	38	32	23.5
80	80	78	77	75	73	71	69	67	65	62	59	56	53	50	45	40	35	32	20
75	75	73	72	70	68	66	64	62	60	58	55	52	49	45	41	36	32	25	16.5
70	70	68	67	65	63	61	59	57	55	53	50	47	44	40	37	32	28	22	13
65	65	63	62	60	59	57	55	53	50	48	45	42	40	36	32	29	24	18	10
60	60	58	57	55	53	52	50	48	45	43	41	38	35	32	29	25	20	14	6
55	55	53	52	50	49	47	45	43	40	38	36	33	32	28	25	21	16	11	3
50	50	48	46	45	44	42	40	38	36	34	32	30	27	24					
45	45	43	42	40	39	37	35	33	32	30	28	26	21						
40	40	39	37	35	34	32	31	30	27	26									
35	35	34	32																
32	32																		

Read the air temperature in the left hand column and the humidity at the top of the chart. The intersection of the two shows the dew point or the point at which water will condense on a surface with the corresponding temperature.

If the temperature in a facility is 75º F (24º C) and the relative humidity is 35%, the intersection of the two shows that the Dew Point is reached at a temperature of 45º F (7º C), or below. This means that moisture vapor in the 75º F / 35% RH air will condense on any surface that is at or below the Dew Point temperature of 45º F.

Source: Building Performance Solutions www.buildwithbps.com

5. For shipping from the customer's plant to the final location, the product again needs to be protected, especially if product parts are in intimate contact with each other. When this is the case, the product is very susceptible to storage stain, if surfaces become wet.
    a. Paper wrapping is one way to protect product while in transit or during storage at a jobsite. Be careful to not wrap bundles of sheets if wet. This traps moisture and prevents drying.
    b. Do not wrap bundles of sheets tightly in plastic. Allow the product to "breathe" by providing air circulation.
    c. Store the lifts of sheets indoors if possible.
    d. Store the panels above ground by at least 12 inches to allow air circulation beneath the bundle. If bundles are stacked, ensure free circulation of air between bundles using cured lumber spacers.
    e. Inspect frequently to assure that the product has not become wet.
    f. Elevate one end of a bundle of sheets to allow water to drain if moisture gets into the lift. Make sure there are no low spots along the length so as to allow water to flow freely if necessary.

Treatment of Galvanized Steel Damaged by Storage Stain

Galvanized sheet damaged by storage stain generally cannot be restored to its original high lustre appearance. The stain, depending on severity, irreversibly alters the surface characteristics of the zinc to varying degrees. Nevertheless, there are treatments that are helpful in improving the appearance, depending on the severity of the stain.

1. For less severe initial white rust, rub/brush the surface with a mixture if mineral oil and sawdust. The mild abrasive action may remove the stain, although this treatment is not of much help for advanced wet storage stain. Many users have found that if lightly stained panels are used as is, the stain "weathers off" after being exposed to the outdoor environment for a year or so, depending on the location.
2. If the stain is not too severe, it may be removed by washing with white vinegar, followed immediately by a thorough rinsing with water to neutralize the surface. The removal can be assisted by the use of a stiff nylon brush. The sheets must be dry before restacking. This treatment will remove some of the metallic lustre from non-stained areas, but not to an excessive degree.
3. Other commercial products that will clean white rust in a manner similar to white vinegar are: CLR®, lime juice, Naval Jelly® Rust Dissolver, and Picklex™ 10G.[3] Another product that has been reported to clean white rust is Bar Keepers Friend®, which is oxalic acid-based.
4. For more severe staining, a solution of 5% (by volume) of phosphoric acid in water, with a wetting agent added, can be brushed onto the sheets. The sheets must be immediately well rinsed to neutralize the surface and then thoroughly dried. This treatment will remove most of the metallic lustre, even in non-stained areas.
5. If the stain has progressed to dark grey or black in color, removal is probably not possible.
6. One method of restoring the protective value of the zinc coating, and improving the appearance of storage stain-damaged sheets, is to apply a good, color matched, zinc-rich paint. The surface must be thoroughly cleaned using any of the products described above, brushed, rinsed and dried beforehand. After two years or so, weathering will largely remove any difference in appearance between the zinc-rich paint and the galvanized surface.

Two excellent references that were consulted when preparing this article and that discuss storage stain in greater detail are:

[1] Zhang, Xiaoge Gregory: Corrosion and Electrochemistry of Zinc, Plenum Press, New York, 1996, pp. 236-239.
[2] Porter, Frank C.: Corrosion Resistance of Zinc and Zinc Alloys, Corrosion Technology Series, Vol. 6, P.A. Schweitzer (ed), Marcel Dekker, New York, 1994, pp. 64-66 and 372-373.

Summary

Storage stain, or white rust, is the surface corrosion that occurs on galvanized sheet when wet while tightly bundled (in coils, or in lifts of blanked sheets/roll-formed panels), and then not immediately separated and allowed to dry. The continual wetness prevents the formation of a protective passive film on the zinc surface. The result is a stained, discolored sheet for which it is virtually impossible to return to its original shiny metallic appearance.

To prevent white rust, galvanized sheet must be protected from contact with moisture whenever the sheets are in close contact (coiled or bundled) and free airflow is not available to dry the surface.

---

[1] Katsuya, H., Oikawa, K., Tanimoto, W., Nagoshi, M., Koba, M., *Segregation Mechanism of Al-based Oxides on Surface of Zn-0.2%Al Hot-dip Galvanized Steel Sheets*, ISIJ International, Vol 60, (2020), No.8, pp. 1765-1773
[2] Smits, R.P.J.M., Smeulders, J.B.A.F., *Surface Chemistry-Based Defects on Steel Sheet*, Investigated by SEM/EDS, IRON & STEEL TECHNOLOGY, AIST.ORG, FEB 2017
[3] Duran, B., Langill, T., *Cleaning Wet Storage Stain from Galvanized Surfaces*, 2007, American Galvanizers Association