Performance Characteristics of Zinc-Nickel Alloys and Dip Spin Coatings for Fastener Applications

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As the performance criteria for plated fasteners have increased, directives to meet strict environmental considerations has forced sweeping changes to surface finishes. The resulting field performance has been as varied as the alternatives. This paper will compare zinc-nickel alloy plating and dip spin coating technology in regards to various critical performance characteristics for automotive fastener applications. Corrosion resistance, total friction coefficient and contact with dissimilar metals among other key properties will be discussed.

Keywords: *automotive fasteners, zinc-nickel plating, dip spin coating, corrosion resistance, torque tension*

Comparison between Zn-Ni electroplating and dip spin

In today's competitive market place, consumers require higher quality products than ever before. Automobiles are used under severe conditions, especially in regions such as North America and Europe. During the winter, salt is used to prevent and/or melt road ice. In the summer, sand particles cause erosion, which plays a role in initiating cavities. Dipsol of America provides several zinc-alloy plating processes for fastener application which offers better performance in highly corrosive environments. This paper compares the performance of Zn-Ni alloy electroplating with dip spin applications.

General alloy plating characteristics for corrosion performance

More than 100 different practical electroplated alloy processes have been invented since a zinc-copper alloy process was developed in 1841. The merits of alloy plating are as follows:

- New phases can be produced which do not exist on metallurgical alloy phase diagrams.
- Alloys can be produced which are unobtainable by thermal methods, such as an alloy between a high melting point metal and a low melting point metal.
- A high performance deposit film can be produced in a thin coating.

When considering an alloy coating for the corrosion protection of steel, the following features should be taken into account:

- Corrodes sacrificially to steel.
- Stability of its corrosion products.
- Allows the formation of an adherent chromate conversion film.
- Slow dissolution of the chromate film when exposed to salt solution.

Corrosion of steel plated with Zn or Zn alloy

By plating deposits of zinc and zinc alloys on a steel substrate, the steel will be protected. Because of their oxidation potentials with respect to steel, zinc and zinc alloys sacrificially dissolve with respect to iron. As shown in Fig. 1, the corrosion performance of pure zinc is compared to that for several commonly used zinc-based alloys. In general, a zinc alloy plated finish on steel exhibits very good corrosion performance in neutral salt spray.

Of the two zinc-nickel alloys shown in Fig. 1, the coating containing the higher amount of nickel (12 to 16 wt% Ni versus 4 to 10 wt% for the lower nickel content alloy) shows the better corrosion performance. This effect is seen more clearly in Fig. 2, as the oxidation potential gets closer to that of the steel substrate (Fe) with increasing nickel content in zinc-alloy deposit. The corrosion performance improves with higher amounts of codeposited nickel. Previously, as determined through testing, the maximum corrosion performance was attained at 15 wt% Ni, as the oxidation potential was more noble. Fortunately advances in conversion coating technologies have allowed the formation of adherent chromate films on zinc-nickel deposits containing over 16 wt% Ni, giving even higher corrosion performance.

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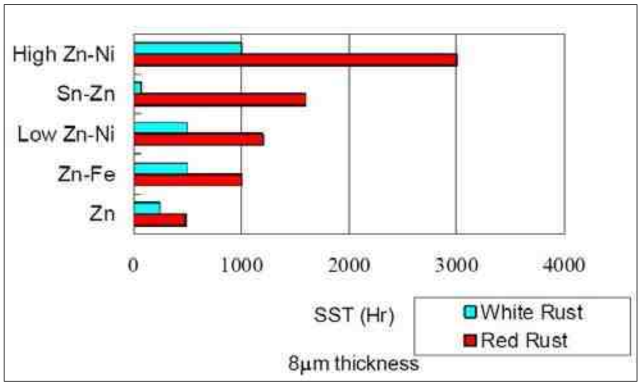

Figure 1—*Neutral salt spray (NSS) corrosion performance for zinc and a selection of alloy electrodeposits.*

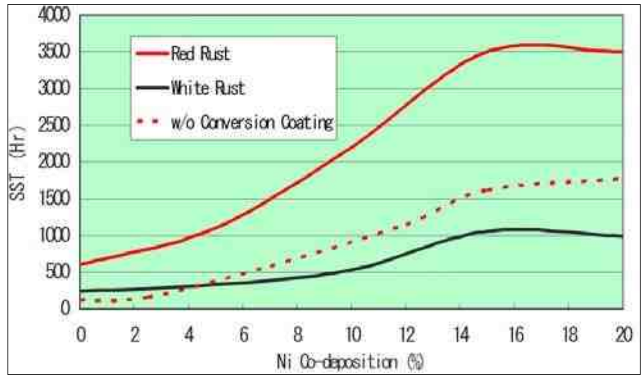

Figure 2—*Neutral salt spray (NSS) corrosion performance versus zinc-nickel alloy composition, in terms of wt% nickel.*

Figure 3 shows the corrosion potential difference between conventional zinc, low nickel Zn-Ni (4 to 10 wt% Ni) and high nickel Zn-Ni alloy (12 to 16 wt% Ni). The potential of zinc is -1.1 V_{SCE} and the driving force is too large for effective sacrificial protection. The addition of nickel reduces the excess driving force but still provides sacrificial protection.

The crystal structure of the higher nickel alloy deposits are uniform and consist of a single structure. The low nickel Zn-Ni alloy electrodeposits exhibit a dual-phase crystal structure. Further, it provides the means for localized galvanic cell corrosion. Referring to the x-ray diffraction plots in Fig. 4, the low nickel Zn-Ni alloy deposit contains the two phases, Zn and Ni_3Zn_{22} (δ phase). The high nickel Zn-Ni alloy deposit only has Ni_2Zn_{11} (γ phase).

The corrosion products are very stable in corrosive environments. Referring to the x-ray diffraction plots in Fig. 5, basic zinc chloride is formed on the surface of the Zn-Ni alloy deposit, providing a barrier film with high electrical resistance and a lower dissolution rate. In comparison to the corrosion rates of pure zinc, low Zn-Ni and high Zn-Ni in Table 1 exhibit a corrosion rate for high nickel Zn-Ni alloy that is 1/50 of the rate for conventional zinc.

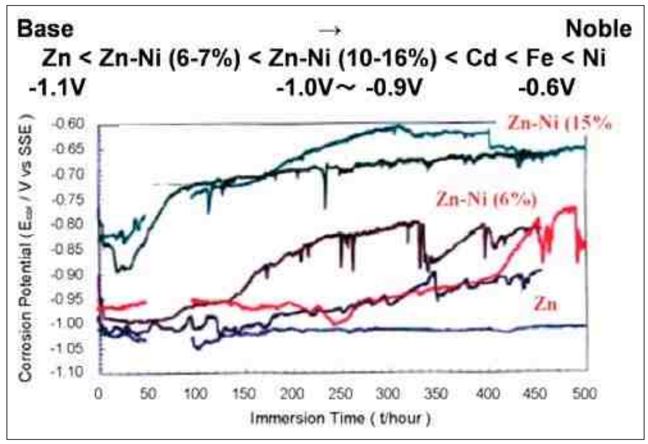

Figure 3—*Corrosion potential diagrams (in 5% NaCl solution).*

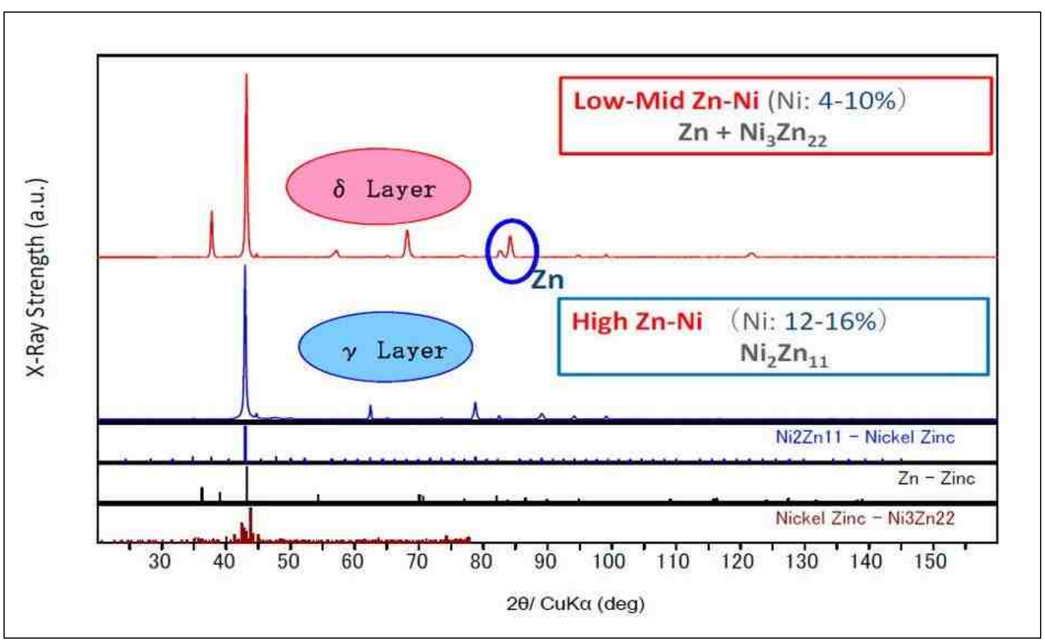

Figure 4—*Crystal structure of plating deposits (by XRD).*

Table 1

Corrosion rate data

	Zinc	Zn - 7% Ni	Zn - 15% Ni
Metal density (ρ), g/cm^3	7.14	7.26	7.40
Nyquist plot charge transfer resistance, Ω	500	5,000	21,300
Corrosion current, A	4.2×10^{-5}	4.2×10^{-6}	9.8×10^{-7}
Corrosion rate, μm/ month	51	5.0	1.2

Table 2

Deposit hardness

Non-cyanide zinc	100 - 140 VHN
Acid chloride zinc	60 - 80 VHN
Acid zinc-cobalt	180 - 210 VHN
Acid zinc-nickel	140 - 180 VHN
Alkaline zinc-nickel	250 - 310 VHN
High %Ni zinc-nickel	250 - 450 VHN
Alkaline zinc-iron	100 - 140 VHN
Tin-zinc	100 - 140 VHN

Corrosion resistance performance

Figure 6 shows the results of a neutral salt spray corrosion test comparison between conventional zinc, low nickel Zn-Ni and high nickel Zn-Ni alloys. Each panel was indented with a standard 8-mm Erichsen cup test normally used for sheet metal formability. It can be seen that the high nickel Zn-Ni alloy has good corrosion performance, even in the deformed area.

Mechanical properties

Due to the presence of nickel metal in the electrodeposit, Zn-Ni alloys have a higher hardness, as shown in Table 2. This higher hardness offers improved scratch-resistance.

The high nickel Zn-Ni alloy deposits were also subjected to a severe 90° bend test and then exposed to neutral salt spray testing. No red rust was observed after 3000 hr of salt spray, as shown in Fig. 7.

Studies of deposit stress, as shown in Fig. 8, indicate that the high nickel Zn-Ni alloy exhibited only very minor tensile stress, which poses no concern in service.

Performance comparison between Zn-Ni alloy and dip spin coatings

The next phase of work involved a comparison of the performance of alkaline high-nickel Zn-Ni electrodeposits with dip-spin coating systems, which have shown promise in fastener applications. A proprietary chromium-free dip spin process,** composed of zinc and aluminum flakes in an inorganic binder, was used in this comparison.

Both alkaline high nickel Zn-Ni alloy and the dip-spin coating provide a higher level of corrosion protection in terms of salt spray protection. However, as shown in Fig. 9, the zinc-nickel performance advantage becomes evident when subjected to cyclic corrosion testing. Many consider cyclic testing to be more representative of field performance.

The corrosion resistance advantage of zinc-nickel alloy is based on its fundamental electrochemical potential difference with respect to steel. This results in a coating that is sacrificial to steel thus protecting the functional performance of the part, which is paramount for fastener applications (Table 3).

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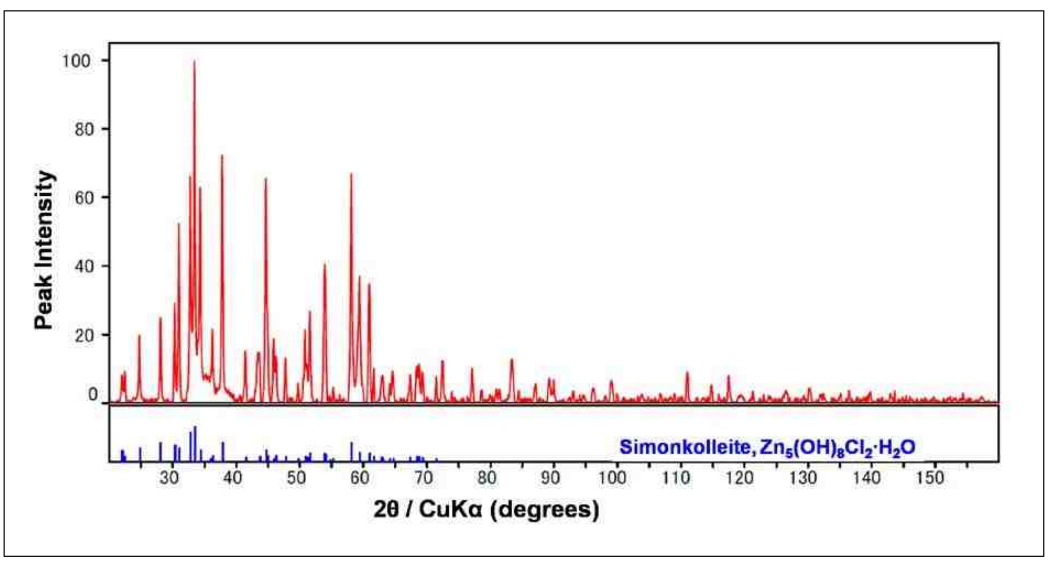

Figure 5—*X-ray diffractin plot of corrosion products formed on Zn-Ni deposits.*

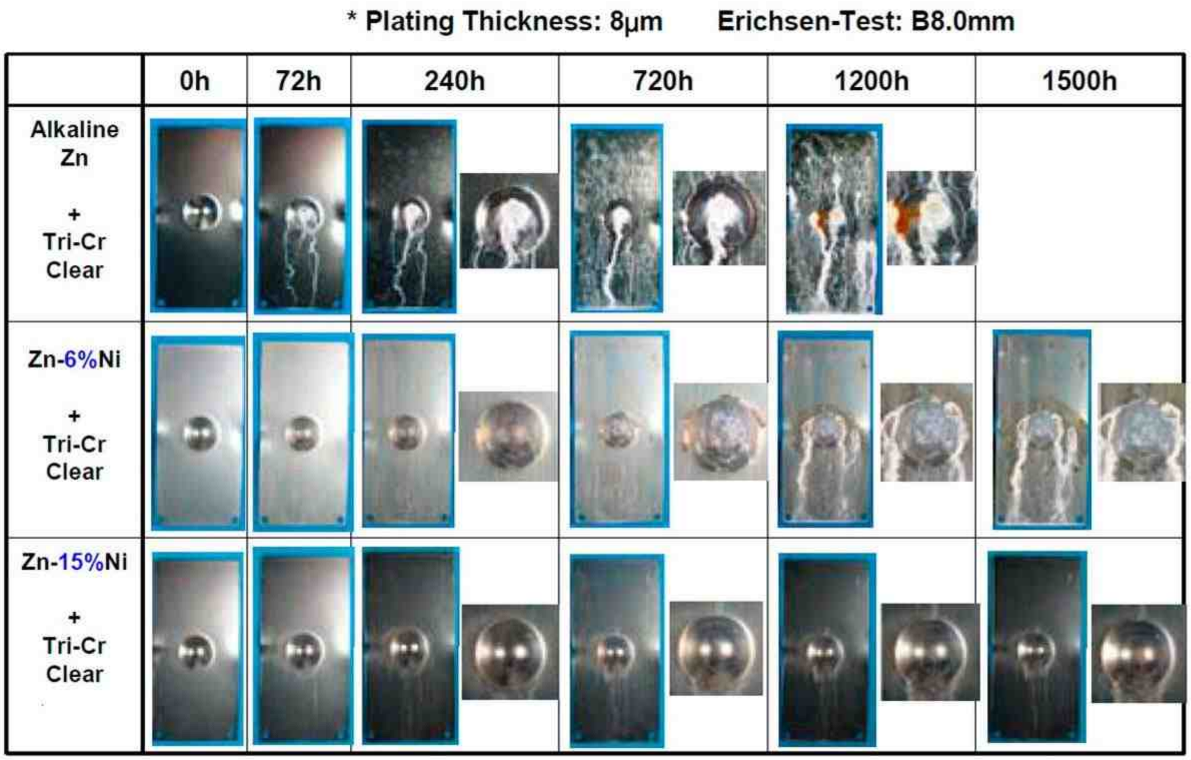

Figure 6—*Erichsen cup test results after neutral salt spray (NSS).*

Figure 7—*Bend test results after 3000 hr neutral salt spray (NSS).*

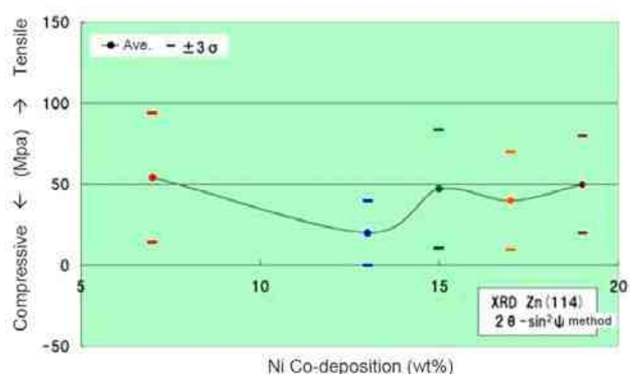

Figure 8—*Stress test results.*

A dip-spin type coating, as indicated in Table 3, works as a barrier film to protect the base part or substrate. As with all barrier coatings, performance can be excellent. However its performance relies heavily on the continuity of the barrier layer. Much has been done to try and improve the coating's susceptibility to reduced corrosion resistance whenever the barrier layer is damaged, but this issue remains a significant problem, particularly in volume production.

Torque tension is particularly important in fastener applications. As shown in Fig. 10, torque-tension values for both zinc-nickel alloy plating and dip-spin finishes are achievable for most desired requirements.

The rapid advancement of organic polymer or friction-modifying topcoats enables them to be applied and bonded to either finish. Zinc-nickel alloy plating on a production scale provides more consistent torque and corrosion resistance properties. This is largely due to the smooth, consistent finish over the entire part, especially in threaded areas, when compared to dip spin applications, which can suffer from significant variances, as seen in Fig. 11. Zinc-nickel alloy is free from the head and thread fill issues encountered with dip-spin coatings.

Table 3

Comparison of Zn-Ni versus dip-spin characteristics

	Film formation	Post treatment	Film structure	Corrosion resistance mechanism
High %Ni zinc-nickel	Electroplating in aqueous solution at room temperature	Trivalent Cr conversion coating	Zn-Ni alloy uniformly distributed; $Zn{\cdot}Ni_2Zn_{11}$ (γ)	Zinc sacrificial protection plus anti-rust compound made of Zn·Ni
Dip-spin coating	Dip coat paint and bake to dry (>200°C)	Organic polymer top coat or friction modifier	A type of paint made of metal flake and a silicon-series inorganic binder.	Coating film works as a barrier layer.

Figure 9—*JASO (Japanese Automobile Standards Organization) cyclic corrosion test results; (Salt Spray 35ºC/4 hr ?? Dry 60ºC/2 hr ?? Humidity 95%/ 50ºC/2 hr).*

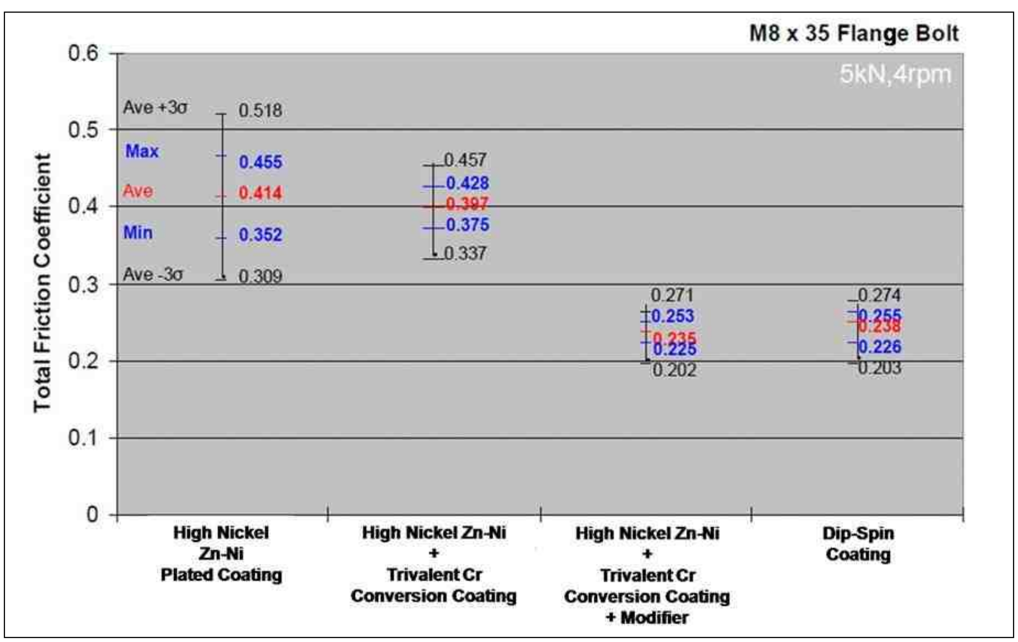

Figure 10—*Torque tension test results.*

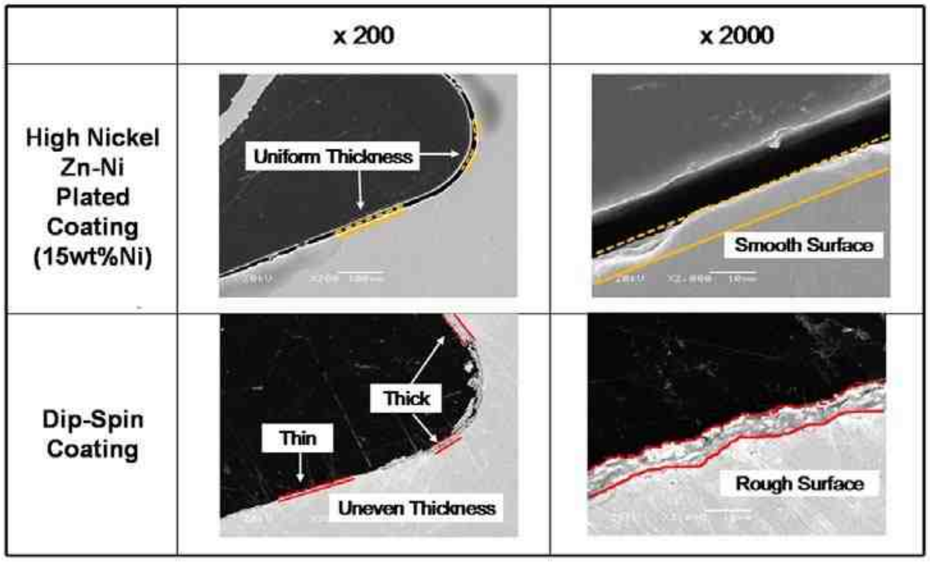

Figure 11—*Comparison of zinc-nickel and dip-spin cross-sections (bolt thread section).*

Conclusion

There is a long track record of performance for both alkaline zinc-nickel alloy plating and dip-spin coating technology. Alkaline zinc-nickel coatings involve an electroplating process and therefore provide a smooth, more uniform finish when compared to dip-spin coatings. High alloy alkaline zinc-nickel coatings maintain stable performance even after aging and can use conventional plating equipment. The above attributes, combined with zinc-nickel being a truly sacrificial coating, make it an ideal choice for peak performance fastener plating.

About the author

Dr. Toshi Murai is President of Dipsol of America Inc. He has worked for Dipsol since 1977, when he began with Dipsol Chemicals Co., Ltd (Tokyo, Japan). He has been working at Dipsol of America since 1993. His time with Dipsol has involved research and development on a variety of metal finishing processes, including alkaline and acid zincs, zinc-nickel alloys, neutral tin-zinc alloys and chromate conversion coatings.

Fact or Fiction?

Continued from page 29.

to present both sides [of the global warming theory] as though it were a question of balance.'"[3]

Some final thoughts:

So there you have it. Media alarmism, like climate itself, runs in cycles.[4]

Catastrophic manmade global warming:
1981-present
Catastrophic manmade global cooling:
1954-1976
Catastrophic global warming:
1929-1969
Catastrophic global cooling:
1895-1932

In spite of all the media reported consensus on global warming, here are some words from Jonathan Margolis that are worth thinking about: "Any statistician trying to extrapolate a million-year trend from a hundred years' numbers would be castigated for working too limited a sample. Furthermore, the hundred or so years of temperature records on which we are forced to base the heating hypothesis are admitted, even by global warming proponents, to be patchy in reliability. Some of the latest satellite tracking of atmospheric and surface temperatures, additionally, fails to show any clear warming trend. The very contention that a relatively puny species, a troop of glorified apes which could still fit shoulder to shoulder on to a scrap of land the size of the Isle of Wright, off southern England, has damaged, and without particularly trying to, something as vast as an entire planet will strike many as an especially audacious example of the arrogance of the present. The twin idea that we can rescue the planet does not seem much less conceited."[5]

So where are we today? In the midst of all the hype about global warming, have you heard about the glitch that's been encountered? After nine years of non-warming, the planet actually began to cool in 2007 and 2008 for the first time in 30 years. The net warming from 1940 to 1998 had been a minuscule 0.2°C. The UK's Hadley Center says the earth's temperature has now dropped back down to about the levels of 100 years ago. "There has been no net global warming within living memory," says Dennis Avery.[6] Add to this the fact that, so far, 2009 doesn't look like another barn-burner for the warming advocates.

Guess What? Perhaps the next scare will be an impending Ice Age. Are you surprised? *P&SF*

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