

## FROM THE EDITOR

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# Seren-ZDDP

Life is full of accidental discoveries.

## WHAT DO ASPIRIN AND ZDDP HAVE IN COMMON?

Both were developed to treat one issue but were found to be even more effective in dealing with a relatively greater issue. They also are examples of serendipity.

The word serendipity was invented by writer Horace Walpole in 1754. He was alluding to a fairy tale, The Three Princes of Serendip, whose heroes "were always making discoveries, by accidents and sagacity, of things they



The Three Princes of Serendip 'were always making discoveries, by accidents and sagacity, of things they were not in quest of.' (Photo courtesy of <https://strawberryindigo.wordpress.com>.)

Interestingly the Union Oil patents refer to a previous patent application in 1937, but this cannot be traced. Thus it seems probable that ZDDPs were first used in engine lubricants in the late 1930s.

"The antiwear properties of ZDDP remained apparently unnoticed throughout the 1940s. In 1949 however, V8 engines having overhead valves and increased compression ratios were introduced, resulting in greatly increased stresses on

were not in quest of." Serendip, or Serendib, is the ancient name for Ceylon (the island country now known as Sri Lanka).

The antithrombotic (blood clot prevention) effects of aspirin were discovered serendipitously. Shortly after John Lister (for whom Listerine antiseptic mouthwash is named) pioneered the use of phenol as an antiseptic in surgeries, scientists sought to develop a drug that could be used to similar effect on patients suffering from bacterial diseases. In the 1870s, salicylic acid was synthesized and administered since it was known to produce phenols in the body. In this form, it had anti-febrile (fever reducing) properties but would not reduce infection, and it caused nausea.

In 1897 Bayer chemist Felix Hoffmann prepared an acetyl derivate with fewer undesirable side effects and an analgesic (pain reducing) effect. It was named aspirin because the salicylic acid had originally been obtained from *Spiraea* plants, with the prefix *a* to denote acetyl.

In 1948 Dr. Lawrence Craven prescribed daily doses of aspirin to 400 patients, and in 1950 he reported that none had suffered

a myocardial infarction (heart attack) during that two-year period. It took many more years of study to evaluate and accept the antithrombotic effects of aspirin, mostly after Dr. Craven's ironic death in 1956—by myocardial infarction.

In the case of ZDDP, it is its antiwear characteristics that were discovered serendipitously. The story is told well in STLE-member and Imperial College professor Hugh Spikes' 2004 Tribology Letters paper, The History and Mechanisms of ZDDP.

He states, "ZDDPs first appeared formally on the lubricant additive stage in 1941 with the filing of four patents, one by the company Lubri-zol (the name remained hyphenated until 1943), one from American Cyanimid and two from the Union Oil Co. The Lubrizol patent concerned ZDDPs having cyclohexyl-based alkyl groups and the one from American Cyanimid metal dithiophosphates with capryl groups, while the Union Oil patents covered a much wider range of metals and alkyl structures. All three patents claimed ZDDPs as bearing corrosion and oxidation inhibitors in engine oils.

valve train components.

This led to major cam and follower wear problems throughout the U.S., and in 1955 it was found that oils which contained ZDDP generally gave less wear than those without it. The result was a very rapid adoption of ZDDP within the automobile industry and by 1958, as reported by Larson. The compound type zinc dialkyl dithiophosphates has gained wide acceptance in the U.S. for high-quality motor oils. Two out of three of the major U.S. automobile manufacturers either require zinc dithiophosphate at about 1% of an 80% concentrate in the initial fill in new automobiles or require qualification tests which only zinc dithiophosphates can pass."

As you can see, diligent observation of the application of existing technology can occasionally reveal alternate effects with significant ramifications.



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