

CERAMIC REINFORCED TECHNOLOGIES

CERFLON® and CERTEX™ FluoroCeramic Chemistry



CERFLON® Chronological History

A Guide and Manual

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Section VI: CERFLON® Chronological History Booklet



A Chronological Summary of FluoroCeramic CERFLON® Development

- 1986 Howard Leendertsen (HVL) acquires majority interest (80%) in Hilton Oil Corporation (HOC), a Seattle, Washington formulator and manufacturer of industrial and fleet lubricants.
- 1987 HOC began an expansion process to position the company for a broader product offering and increased automotive aftermarket distribution.
- 1988 Continued to look for new chemistries to broaden line. Learned of Acheson Colloids three year long project to develop a stable colloidal dispersion of PTFE in a highly refined petroleum oil.
- 1989 Acheson produces the first commercially available PTFE colloidal dispersion and HOC is the first to use it as a solid lubricant additive for industrial lubricants and then for automotive applications. At that time, it appeared these dispersions should be further evaluated as the possible successor to the graphite solid lubricant additives that were used in the “fuel economy” motor oils of the 1970’s (ARCO Graphite). HOC also saw this as an opportunity to create a relationship with DuPont and use the powerful Teflon® brand to introduce a new line of products along with the credibility of the DuPont oval on the products and collateral material.
- 1990 DuPont grants HOC the right to use the Teflon® trademark and DuPont oval trademark. HOC launches “T-Plus”, a well differentiated automotive aftermarket product. The “T” in “T-Plus” stands for Teflon®. T-Plus competed directly with “Slick 50” while it was moving to \$100 MM revenue and marketed itself as a far superior consumer value for these reasons: 1. Multi viscosity (10w30) vs. single grade (30w) motor oil 2. DuPont Teflon® vs. generic PTFE 3. Formulated with stable colloidal dispersion of DuPont Teflon® versus stirred in powders 4. A minimum of 50% more Teflon® than the PTFE in “Slick 50”. 5. Aggressively priced with a minimum savings of \$10 to the consumer for a superior product that carried the marketing statement, “Why Pay More For Less”!
- 1992 HOC’s “T-Plus” achieves broad U.S. distribution and #2 market share in national accounts such as Pep Boys, AutoZone, Wal-Mart, Checker-Schuck’s-Kragen (CSK-now O’Reilly), Advance Auto Parts, Target, Sears, K-Mart, NAPA, True Value and Ace Hardware and many others.
- 1993 Another year of domestic growth and the start of development of global sales for all Hilton products in Southeast Asia and Europe.
- 1994 Worked with DuPont under a Technology Development Agreement to explore and evaluate other fluoropolymers for improved lubricant performance.
- 1995 HOC is made aware of a stable colloidal dispersion of a ceramic, Boron Nitride (BN), by its Japanese distributor, Taiyo Corporation. HOC starts a Research & Development project to see if better Hilton products can be formulated with BN alone but, because of the high cost of BN, it appeared that it would not be economic for most automotive applications. However, Boron Nitride appeared to have properties that could enhance the performance of all of HOC’s
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products, so work continued in an effort to better understand how BN could be used economically. The benefits of BN included improved extreme pressure and load carrying properties, better thermal stability and also a new finding which was its compatibility with the Acheson Teflon® dispersions. Preliminary tests with the Teflon® and BN dispersions indicated that an apparently undiscovered synergy existed between BN and Teflon®. Based on both performance and economics, ladder studies were conducted to determine the best ratio of BN:PTFE. These studies indicated that 80% PTFE to 20% BN was the optimal ratio which also made BN affordable. While work continued on the development of a new generation of industrial and automotive lubricants using BN with, a collateral patent application was filed for the composition and method for pre-treating the internal surface of an engine to remove varnish and neutralize ZDDP, so as to provide maximum sites for PTFE plating (US 5,641,729 - Prep Patent)

In 1995 HOC shareholders were asked by John Barr, then President of Valvoline, to discuss a joint venture or acquisition with or by Valvoline. The discussions went nowhere and HOC management viewed the exercise as a Valvoline “fishing expedition”.

HOC continued research and development projects and now with the benefit of understanding the synergy between PTFE and most other fluoropolymers and BN, HVL filed a patent application for “Ceramic Reinforced Fluoropolymer”. Also in 1995, HOC introduced T-Plus², an advanced product using the new PTFE/BN formulation and the “T-Plus Engine Prep”.

- 1996 Contacted again by John Barr, now President of Quaker State (QS), to reopen discussions. Because of the T-Plus² product introduction at AAPEX in 1996, they are very interested in the chemistry and learn of the patent application. Then QS Chairman & CEO, Herb Baum wanted to introduce a “next generation” motor oil with a “Ceramic Reinforced Fluoroadditive”, so QS tendered an offer to purchase the assets of HOC. HOC was also speaking with the executive and technical team at CASTROL in an effort to better understand the value of the technology to a major oil company. At this time, HVL does not want to sell the “Ceramic Reinforced Fluoropolymer” IP, but it becomes apparent that this would be the deal breaker for a good HOC deal. John Barr pushes for a fast closing and the shareholders of HOC accept the Quaker State offer.
 - 1997 Hilton Oil Corporation’s assets are sold and transferred to Quaker State in February, 1997. As part of the deal, HVL gets a license from Quaker State to practice the technology for all non-automotive applications.
 - 1998 Quaker State continues the “Ceramic Reinforced Fluoropolymer” patent application process and the patent is granted on July 21, 1998 to HVL and assigned to Quaker State. HVL forms Ceramic Reinforced Technologies (CRT) and files for the trademarks Cerflon® and Certex™ and pursues a business model based on licensing a fluoropolymer, Boron Nitride and colloidal dispersion manufacturer to introduce patent protected, trademarked products into non-automotive markets. Also in 1998, Quaker State is acquired by Pennzoil.
 - 1999 Based on work done with Delphi-Harrison Thermal Systems, HVL files a U.S. patent application for “Methods and Apparatus for Applying Liquid Fluoropolymer Solutions to Substrates”. The work conducted at GM demonstrated that coating the internal surfaces of a radiator core with
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a fluoropolymer solution does not degrade the heat transfer or fluid dynamic properties of the radiator. This also translated well into the industrial heat exchange market. (US 6,200,632 CRT - Heat Exchanger Patent)

- 2000 HVL continued market development efforts with the Pennzoil-Quaker State (PQS) license and the CRT trademarks, but finds this difficult without ownership of the patent and the restricted right to practice in the automotive markets. At this point PQS seemed to be unaware of the initiatives Quaker State had for the technology and is not using their intellectual property asset in the automotive markets, as intended by Quaker State.
- 2002 HVL meets with Pennzoil Board and repurchases the patent. Under the terms of the new agreement, Pennzoil is granted a royalty free and non-exclusive license to practice the technology. However, under the QS purchase and sales agreement there is a royalty due to the former shareholders of HOC based on a percentage of any lubricant sales using the IP up to a cap of \$5.0 MM. (Pennzoil is now Shell Pennzoil Quaker State). Soon after the patent is reacquired, CRT signed license agreements with Acheson Colloids - now Henkel, Carborundum - now Saint-Gobain Ceramics and ICI Fluoropolymer - now Asahi Glass Fluoropolymer. (In 2013, Henkel is the only current and non-exclusive licensee.)

To Present:

Work continues with establishing markets FluoroCeramic Cerflon® powders to complement the Henkel Cerflon® dispersions. CRT has also developed Cerflon® dispersions in organic solvents (synthetic esters) and is in the final development phase of stable PAO Cerflon® dispersions.

There have been and are many other uses of the composition of matter “Ceramic Reinforced Fluoropolymer” patent. One such example is the 2008 Xerox US Patent Application - US 20080166643 using Cerflon® technology. In the Xerox application, the Henkel SLA 2010 and 2020 Cerflon® dispersions are cited numerous times and outperformed Solvay Fluorolink S-10 (PFPE) that was also evaluated.

CRT has also published a manual: **Boron Nitride & Fluoropolymers – “Cerflon®: The Complete Manual”**. It presents a comprehensive overview of CERFLON® FluoroCeramic dispersions and powders and their value added properties. The manual also discusses the “Ceramic Reinforced Fluoropolymer” composition of matter patent (US 5,783,308) as well as application patents using the CERFLON® technology. Included, as well, are academic papers and examples of commercialized products using the technology.

In 2012, CRT began work with Paul Bessette. Paul is currently President of Triboscience & Engineering, Inc. and lead tribologist for CRT. As such, he has formulated the Cerflon® synthetic ester dispersions and is developing the PAO dispersions. Paul has been involved with synthetic lubricants for over thirty-five years and within that time he spent twenty-four years at Nye Lubricants and three years at Ciba-Geigy. He was honored with the NLGI Fellows Award, Meritorious Service Award, Achievement Award, Clarence E. Earle Memorial Award and Author’s Award. He was Associate Editor for Tribology, Transaction, Journal of Synthetic Lubricants and peer review for NLGI. He is also a member of STLE and ASTM.
