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FROM HEAVY DUTY LUBRICANTS TO BIOBASED FLUIDS – LEGACY OF JOSEPH PEREZ

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Abstract: Advancement in lubricant technology is driven by technical demands, oil market, innovations from related chemical areas and other conventional factors. Nevertheless, a personal impact of an individual scientist can also be very important. Few individuals can claim to have accelerated lubricant progress more than Dr. Joseph M. Perez, who initiated many new developments in lubricant technology and drove them to large scale implementation. Early in his career at PennState he worked on aerospace lubricants, developing highly efficient additives for supersonic planes. When working at Caterpillar he dealt with hydraulic fluids, gear oils and many heavy duty lubricants. During employment at NIST and upon return to PennState Dr. Perez realized the importance of vegetable oils. He pioneered many research directions for their applications, becoming directly involved in vegetable-based engine oils, hydraulic fluids, greases, biodiesel, elevator fluids and many other areas. His innovative thinking, enthusiasm and initiatives will be sorely missed by lubricant researchers.

Keywords: Vegetable Oil; Hydraulic Fluid; Wear; Oxidation

1. INTRODUCTION

Tribology as a science is quite young with just 50 years elapsed after coining its very name [1]. Although most of basic laws in tribology were conceived much earlier, comparatively recent contributions from relatively few researchers helped greatly to shape tribology into a viable multidisciplinary science. Dr. Joseph Manuel Perez Sr. (1930-2016) certainly belongs to a select group of researchers, whose findings and initiatives were very helpful in advancing tribology to the current status. His lifetime achievements were specifically highlighted during the World Tribology Congress in 2017, Soc. of Tribologists and Lubrication Engineers "STLE Fellow" award and through other tokens of recognition. This report presents key concepts, promoted by Dr. Perez, and their influence on tribology.

His exposure to tribology began with his graduate studies in Petroleum Refining Laboratory at Pennsylvania State University (PennState). He was advised by renowned tribologists Merrell R. Fenske and Elmer E. Klaus. After receiving his doctoral degree in 1964 Dr. Perez devoted his career at Caterpillar Inc., National Institute of Standards (NIST) and PennState to tribology and lubricants. He was exposed to many diverse aspects of lubricant technology, ranging from aerospace applications to heavy duty equipment and biodegradable oils. In many cases Dr. Perez would conceptualize a new innovative approach to resolve a lubricant problem and drive the whole research process until full commercialization. Remarkably, he would be able to keep nearly all information about formulation and even application confidential. Nevertheless, lubricant technology benefited from his research significantly. His vision and strong fundamentals provided not just the means to resolve a given issue, but also an explanation why a lubricant problem had occurred and what physical or chemical mechanisms helped to resolve it. Dr. Perez was an innovator and the key driver of many concepts in lubricant technology, which are commonplace nowadays but appeared very challenging initially. These include thin film degradation testing, sequential wear tests, diamond-like coatings, vegetable oil basestocks and many others. Some of these concepts are detailed below.

2. SYNERGY OF LUBRICITY ADDITIVES AND BASESTOCK

Lubricant performance in reducing wear is mostly dictated by Anti-Wear (AW) additives, although basestock is also very important. Various tests are employed to better predict end-use performance, e.g. four ball wear test (4-ball) for hydraulic fluids or engine oils. However, it is hard to relate the test

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duration, such as 2 h in 4-ball, to the actual service life like 5000 h for hydraulic fluids. Bench tests often make it easy to identify poorly performing additives or formulations. However, when the wear rates are low, differentiation between well formulated samples becomes very challenging. Dr. Perez actively promoted the concept of 'sequential 4-ball', which was developed with his personal involvement, although originally reported by E. E. Klaus [2]. The concept represents a three-step sequence: 1) running fresh lubricant and measuring the wear scar; 2) pouring back used lubricant and measuring the scar and 3) replacing the lubricant with its additive-free basestock and measuring the scar, Fig. 1.

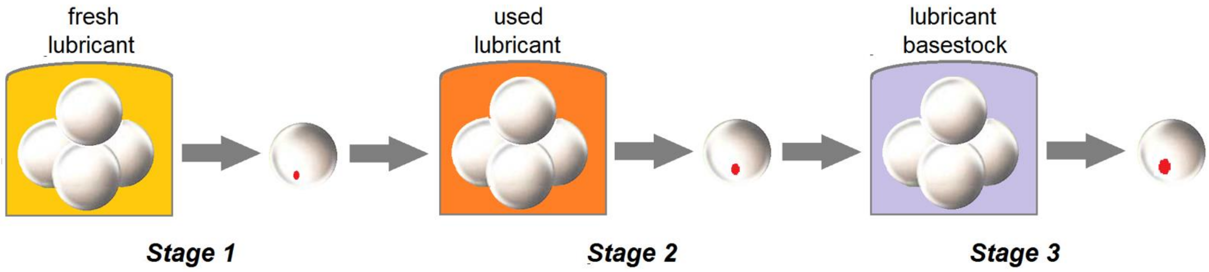

Figure 1. Procedure of sequential 4-ball wear test, using three stages with intermediate wear scar measurements. Synergistic additives should result in little wear scar increase after stages 2 and 3.

Stage 1 was devoted to tribofilm formation. Initially, run-in wear would result in rapid propagation of the wear scar. However, effectively performing synergistic AW additives should eventually reduce wear rates to steady-state. If lubricant is formulated properly, towards the end of Stage 1 only tribofilm is worn out and immediately replenished by AW additives without further wear of steel substrate. After measuring the wear scar, the same used sample is poured back into the same assembly and the test continued into the Stage 2. If no wear increase is observed, it can be claimed that well-performing tribofilm was formed. Then the sample lubricant is replaced with additive-free basestock and the test continued as Stage 3. This stage simulates additive depletion after long service. If wear increase is minimal, it can be expected that the basestock effectively contributes to tribofilm performance. Well formulated lubricants with synergistic additives show essentially no increase in wear scar diameter after Stage 2 and Stage 3 [3].

Obviously, sequential 4-ball parameters can be adjusted as necessary for the final application. Dr. Perez suggested 30 min intervals at 75 °C and 600 rpm with 147 N load, focusing on "delta wear", which is the difference between the measured wear scar diameter and Hertz elastic indentation (at 147 N load D_{HZ} = 0.27 mm on AISI 52100 steel balls of 12.7 mm OD) for hydraulic fluid applications [4]. For engine oils 392 N load was more relevant (D_{HZ} = 0.30 mm). Other types of wear tests, not only 4-ball, could also benefit from a 'sequential' concept and this approach is already used in lubricant technology.

3. LUBRICANTS FOR SEVERE ENVIRONMENTS

In many applications lubricants must endure exposure to high temperatures and aggressive atmosphere, such as industrial application or aerospace. Lubricant durability is usually tested by heating its bulk volume and bubbling gas through it with some metal plates immersed for catalyzing the degradation. However, such tests are usually long and labor-intensive. Dr. Perez and co-workers realized that most degradation takes place not deep into the bulk liquid, but within thin films on metal surface. Large surface area per given volume assures much higher exposure to the atmosphere and metal surface, compared to the bulk liquid. Diffusion limitations become insignificant and degradation proceeds much more rapidly. Again Dr. Perez directly participated in the development of the thin film methodology, which was later published by E.E. Klaus et al [5] as "PennState micro-oxidation".

The methodology allowed rapid assessment of lubricant resistance to thermal stress, oxidation and catalytic surfaces, eventually receiving some recognition in industry. Degraded lubricant film was screened by dissolving it in tetrahydrofuran (THF) or other solvents. Dissolved matter was analyzed by Gel Permeation Chromatography to assess the extent of polymerization, Fig 2. A key parameter was the amount of deposits, which were not soluble in THF. This methodology was used to screen commercial hydraulic fluids and engine oils for some time. Several test procedures became recognized industrially, such as "Caterpillar micro-oxidation". Film thickness variation was one of the problems, because it led to poor repeatability.

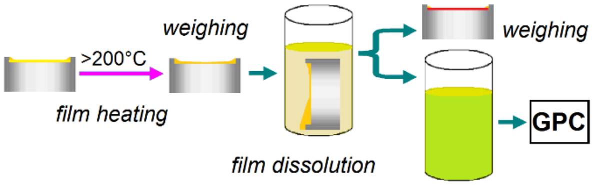

Figure 2. Procedure of "PennState microoxidation" test by heating the film, weighing volatile losses, dissolving the degraded film in solvents and analyzing the soluble portion with Gel Permeation Chromatography.

Another problem was the need for molten metal bath in order to maintain temperatures up to 300 °C. Therefore, Dr. Perez guided microoxidation through several transformations for easier setup and better reproducibility, Fig 3. Eventually the microoxidation test device was commercialized as K29200 and became instrumental in comparing fully formulated lubricants. This helped to minimize the need for engine tests or hydraulic pump stands, both of which are very costly.

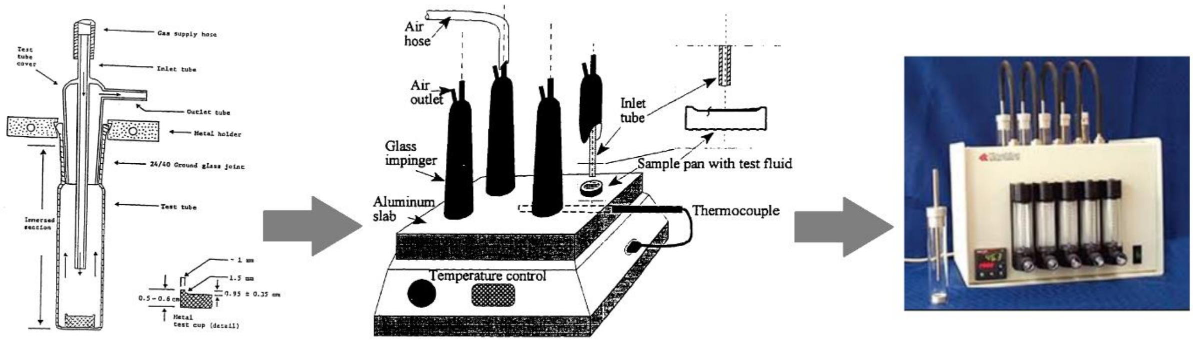

Figure 3. Historical transformation of PennState micro-oxidation test (left, reported in [5]) into a version without a liquid metal bath (center, reported in [6]) and a commercial version K29200 (right, reported in [7]).

Dr. Perez and many of his students used the test to evaluate not only various lubricants [8], but also antioxidant performance [9], innovative surfaces and basestocks [10] etc. He paid particular attention to the testing protocols: which temperature, duration, film thickness and other parameters were the most relevant to the final application. For example, diesel engine oils had to be tested at 250 °C, while internal combustion engine oils at 225 °C. These temperatures were representative of the area near the top ring of the engine piston. Not only microoxidation testing protocols were improved. The thin film concept was successfully utilized in other lubricant degradation tests, Pressurized Differential Scanning Calorimetry in particular.

Lubricants for severe environments were frequented by Dr. Perez. He dedicated significant research to study Diamond-Like Coatings, which now are utilized in many severe applications [11]. Another area where he had significant input was vapor phase lubrication, which was mostly developed by E.E. Klaus [12]. Many of their research results remained unpublished, especially those dealing with aerospace applications. Sequential 4-ball was particularly useful for identifying a tribochemical synergy between Cu soaps and ZDDP in ester basestocks, which later served as a basis for a high temperature application.

4. BIODEGRADABLE LUBRICANTS

A major advancement in lubricant technology took place in the 1990's, when vegetable oils and other biodegradable basestocks were introduced into mainstream lubricants. Dr. Perez was one of the pioneers in this area and successfully utilized his experience in various lubricant applications [13]. Dr. Perez collaborated with startup companies in development of engine lubricants from vegetable oils. Field tests took place in race cars, including ethanol-fueled engines. He also developed several grease formulations with vegetable oil basestocks [14]. Quite early he set up an internship program between

PennState, Caterpillar Inc. and US Department of Agriculture (USDA) laboratories in Peoria to develop biodegradable lubricants. Nearly a dozen of PennState graduate students, post-doctoral and USDA researchers were directly involved in this effort. The program continued for more than 15 years until biodegradable hydraulic fluids and other lubricants became widespread. During this endeavor Dr. Perez and his coworkers introduced biodegradable lubricants for elevators, chainsaws, two-stroke engines and other applications. He thoroughly evaluated environmental effects of disposed lubricants, including their composting [15] and became probably the first researcher to study the compost from lubricants systematically.

Dr. Perez became a strong proponent of biodiesel as fuel. He installed a biodiesel synthesis pilot line in Fenske Laboratory at PennState, operated mostly by students. Various feedstocks, catalysts and processing conditions were tested over a decade. Dr. Perez also investigated lubricity of biodiesel and other alternative fuels [16]. This report does not attempt to describe all of his contributions to tribology. However, it is clear that innovative thinking, enthusiasm and initiatives of Dr. Perez will be sorely missed by former students, colleagues, lubricant researchers and tribologists worldwide.

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