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A CRITICAL ASSESSMENT OF TRIBOPOLYMERIZATION AS AN ANTIWEAR MECHANISM

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ABSTRACT

By tribopolymerization, we mean the planned, intentional, and continuous formation of protective polymeric films on tribological surfaces by the use of minor concentrations of selected monomers capable of forming polymer films "in situ" by polycondensation or addition polymerization. The approach involves the design of molecules which will form polymeric surface films in critical regions of boundary lubrication. The concept has been shown to be effective in reducing wear with ceramics as well as metals in both liquid and vapor phase applications.

The purpose of this paper is threefold, namely:

1. To review our key fundamental research on the topic of tribopolymerization, including more recent views based on measurements of triboelectron emission.
2. To summarize the applications of this concept to a variety of industrial problems, including the use of the compounds in fuels as well as in areas in which environmental issues are important.
3. To briefly outline future plans for fundamental research on tribopolymerization, including theoretical and experimental studies to examine the roles of surface temperature, triboelectron emission, and catalysis on surface polymerization.

KEYWORDS: Tribopolymerization, antiwear additives

WHAT IS TRIBOPOLYMERIZATION?

We define tribopolymerization as the planned, intentional, and continuous formation of protective polymeric films directly on rubbing surfaces by the use of minor concentrations of selected monomers capable of forming polymer films "in situ" either by polycondensation or addition polymerization. The concept represents a rational approach of molecular design to produce thin polymeric surface films in critical regions of boundary lubrication—thus reducing contact, adhesion, and wear.

BACKGROUND

Convincing evidence in support of the idea of "in situ" surface polymerization as a novel approach to boundary lubrication was obtained over 30 years ago, with first results presented at an international conference in Kiev and later published in Wear in 1973 [1]. An important class of antiwear compounds, i.e., partial esters of long-chain dimer acids and short-chain glycols, was shown to be extremely effective as jet fuel lubricity additives and in reducing automotive engine valve train wear. An additive based on tribopolymerization and synthesized by one of the authors while in the Advanced Lubrication Project of Esso Research and Engineering met the stringent requirements of Pratt and Whitney (including Ryder Gear, high temperature stability, filter plugging) and was the first additive to be approved and used commercially in the jet fuel lubricity problem to control fuel pump wear. The concentration used was 0.1 wt.% in jet fuel.

Since then, a great deal of additional research on the concept of tribopolymerization has been carried out in the Tribology Laboratory at Virginia Tech in collaboration with Polish scientists Drs. Czeslaw Kajdas and Roman Kempinski of the Warsaw University of Technology, Institute of Chemistry at Plock, Poland. The cooperation began almost 20 years ago and has continued ever since. Our research focused on two broad classes of compounds namely (a) condensation-type monomers and (b) addition-type (e.g., vinyl) monomers.

THE ACTION OF CONDENSATION-TYPE MONOMERS IN REDUCING WEAR

Although the earlier research dealt chiefly with partial esters of long-chain dimer acids and short-chain glycols—including the monoester of a C_{36} dimer acid and ethylene glycol—further work on condensation-type monomers led to the discovery of other effective antiwear additives, including (a) polyamide-formers including lactams (e.g., caprolactam) and (b) several monomers derived from ring-containing hydroxy-acids and acid esters as well as aminoacids and acid esters. The ring-based condensation monomers were shown to be more effective for higher temperature use. Our studies suggest that the two most important factors governing the action of condensation-type monomers are (a) high surface temperatures and (b) the shape and initial orientation of the molecule on the solid surface.

THE NIRAM CONCEPT AND THE ACTION OF ADDITION-TYPE MONOMERS

It was postulated by Kajdas that the antiwear action of addition-type monomers was initiated by the triboemission of low-energy electrons from the surfaces in contact. This idea stems from the application of his NIRAM (Negative Ion Radical Action Mechanism) approach to tribochemistry. A review of triboemission and its influence on tribochemistry and boundary lubrication was made by Kajdas et al. [2]. To study triboelectron emission experimentally, new research was initiated with the development by Molina of an instrument and

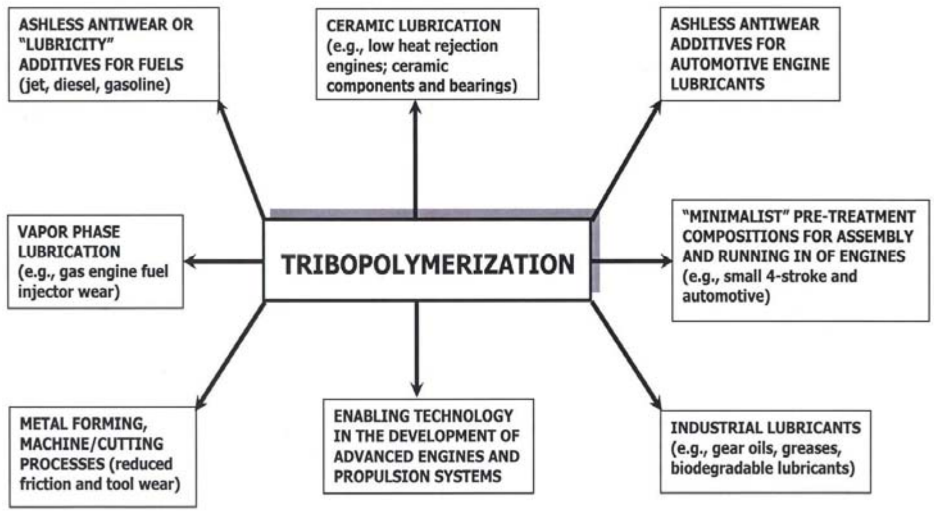

Figure 1. Applications of Tribopolymerization

techniques for measuring triboemission [3]. The research did demonstrate that low-energy electrons are emitted from ceramic surfaces, thus supporting the antiwear action mechanism postulated for vinyl-type monomers.

APPLICATIONS OF TRIBOPOLYMERIZATION

The antiwear compounds developed from the concept of tribopolymerization have been shown to be effective with metals as well as ceramics in the liquid as well as vapor phases. As summarized in Figure 1, there are several proven and possible applications of tribopolymerization technology in fuels, lubricants, special uses, and as an enabling technology in the development of new propulsion systems. The compounds developed are ashless and contain no harmful phosphorus or sulfur. And many are, or can be designed to be, non-toxic and biodegradable. Thus, the applications of this technology are diverse and contain a variety of cost, performance, energy and environmental advantages. To facilitate the use of tribopolymerization technology for practical applications, an agreement of collaboration was recently made among three organizations: Tribochem International, Ltd; the Institute for Terotechnolgy at Radom, Poland; and the Central Laboratory of Petroleum in Warsaw, Poland [4].

PLANS FOR FUTURE RESEARCH AND DEVELOPMENT

A major goal of future research on tribopolymerization is to determine the importance of three factors in initiating the "in situ" formation of protective polymeric antiwear films on rubbing surfaces, namely (a) the emission of low-energy electrons, (b) surface temperatures, and (c) catalysis. The research will involve both theoretical and experimental elements as part of a broader investigation in modelling mechanical, thermal, electrical, and chemical effects in tribo-logical processes. Recent studies by Vick et al. [5] have demonstrated that depending on the metallic system and conditions used, thermionic emission can be expected, thus defining a region in which high surface temperatures and triboemission of low-energy electrons both occur. In addition, the application of chemical modeling techniques, using our CHEM-X® software, and possibly the Virginia Tech supercomputer to examine probable (minimum-energy) orientation of monomers on solid surfaces prior to polymerization, will be explored. Last, we will continue to develop, arrange for, and cooperate in field-testing of promising additives and lubricants for a variety of end-use applications.

CONCLUSIONS

In conclusion, background and key results of fundamental research on the concept of tribopolymerization have been summarized, diverse practical applications of the concept have been described, and plans for further research outlined. Although evidence in support of the postulated mechanisms for the condensation and addition-type monomers has been obtained, the process is more complex than originally envisioned; reactions between the monomers and solid surfaces (both ceramic and metallic) can occur in addition to the formation of long-chain oligomers or polymers. Several questions remain. Limited space does not permit a detailed discussion here of results but an extensive review of our work on tribopolymerization may be found as a chapter in a recent book [6].

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