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Branched alkylphosphinic acids demonstrate explicit anti-wear effect

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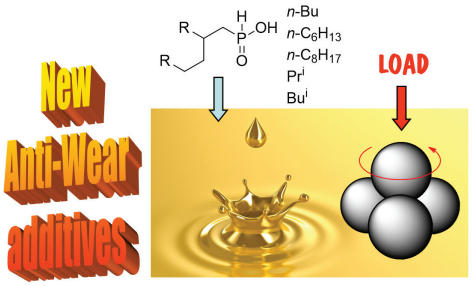
Branched alkylphosphinic acids obtained from synthetically available α-olefin dimers demonstrate promising anti-wear properties and represent a prospective group of ogranic friction modifiers due to high thermal stability.

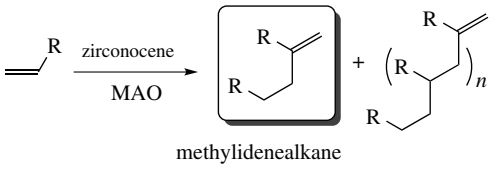


Investigation and development of petrochemical products with enhanced characteristics is topical within the modern chemical science and technology. In recent decades, coordinative oligomerization of α-olefins catalyzed by zirconocene–methylalumoxane (MAO) systems was widely used for the production of motor oils, lubricants and other products with excellent properties that outperform the features of conventional petrochemical goods. Oligomerization of α-olefins can be performed in two routes, as a highly selective dimerization,[1–3] or as a formation of oligomers with a given P_n.[4–8] Vinylidene dimers of α-olefins (methylidenealkanes) are the main products of the former reaction and unavoidable components for the latter process (Scheme 1). Hence, the search for the ways of their chemical modification to obtain valuable products is a highly actual problem.[9–14]

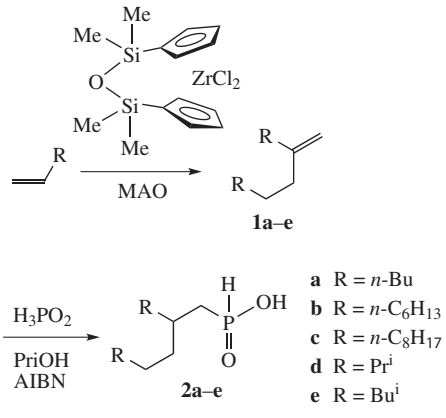
Recently,[15] we reported on the effective transformation of methylidenealkanes to branched alkylphosphinic acids (Scheme 2). These compounds demonstrated higher hydrolytic stability in comparison with traditional phosphates and phosphonates that contain labile P–OR fragment, and were applied as effective rare-earth metal extractants.[15] We proposed that alkylphosphinic acids were capable of binding to the metal surface with a formation of monolayer providing thus anti-wear effect. Such a behaviour is characteristic of amphiphilic organic molecules called organic friction modifiers (OFMs) that inhibit metallic junction growth and thus reduce the extent of solid adhesion.[16]

To date, various organic and organoelement amphiphilic molecules have been used as OFMs, among them, phosphorus-containing atni-wear agents having been represented by phosphates and phosphonates.[17–28] Monohydrogen phosphates and phosphonates containing OH groups are more effective as OFMs in comparison with fully substituted esters due to chemical bonding with a metal surface.[28–30] Generally, the presence of P–alkoxy fragment may reduce the thermal stability of these additives due to thermal retro-ene decay into olefin and phosphorus acid.[17] The ability of ester-based OFMs to decompose with a formation of active acid is beneficial for alkyl carboxylates[31] and trialkyl or triaryl phosphates,[32] but it seems unnecessary for mono/dialkyl phosphates and monoalkyl phosphonates that are able to form lipophilic monolayer on the metal surface.

We proposed that alkylphosphinic acids can be used as thermally stable OFMs. Here we report the preliminary comparative study of anti-wear properties of branched



Scheme 1



Scheme 2

Table 1 The results of four-ball test for 0.5 wt% solutions of **2a–e** in different oils.[a]

Oil	Wear scar diameters/mm					
	none	**2a**	**2b**	**2c**	**2d**	**2e**
PMS	1.15	0.87	1.53	n.d.[b]	0.88	0.85
DOS	0.79	0.73	0.75	0.63	0.68	0.71
PO	0.65	0.46	0.47	0.50	0.55	0.54
PAB	0.64	0.40	0.48	0.40	0.47	0.54
PAO-4	0.80	0.45	0.50	0.45	0.51	0.50

[a]A ChMT-1 four-ball tester (Neftekhimmashsistemy, Russia) was used in 1-hour experiments at 20 °C with 196 N load . [b] Not dissolved.

alkylphosphinic acids obtained from vinylidene dimers of α-olefins. We prepared a number of methylidenealkanes **1a–e** by catalytic dimerization of hex-1-ene, oct-1-ene, dec-1-ene, 3-methylbut-1-ene and 4-methylpent-1-ene, respectively,[2,9] and synthesized a number of branched alkylphosphinic acids **2a–e** by radical addition of H_3PO_2 to alkenes **1a–e** in 2-propanol at 100 °C with continuous addition of 2,2′-azobis(isobutyronitrile) (AIBN) as an initiator (Scheme 2).[†,15]

We evaluated anti-wear properties of compounds **2a–e** (Table 1).[‡] Wear scar diameters were determined for 0.5 wt% solutions of alkylphosphinic acids in base oils of different chemical nature, namely, paraffin oil (PO), polyalkylbenzene oil (PAB), dioctyl sebacinate (DOS), PAO-4 and poly(methyl siloxane) (PMS-300).

In most cases, reducing of the wear scar diameter was detected. The best results were achieved with the introduction of synthesized compounds to hydrocarbon oils, and the smallest decrease in the wear scar diameter was observed in the case of silicone fluid PMS-300. Compound **2c** demonstrated the best characteristics among **2a–e** for oils studied except PMS that was a poor solvent for branched alkylphosphinic acids.

The relationships between the concentrations of alkylphosphinic acid and anti-wear effect were established for the solutions of **2a–e** in PAO-4 (Table 2). Figure 1 demonstrates that the optimal concentration of alkylphosphinic acid in PAO lies in the 0.1–0.5% concentration interval. Acid **2a** was found to be the most promising anti-wear agent. Compounds **2d** and **2e** demonstrated middling characteristics. Acid **2c** prepared from

Table 2 The results of four-ball test for the solutions of **2a–e** in PAO-4.

Alkylphosphinic acid	Wear scar diameter			
	0.1%[a]	0.5%[a]	0.75%[a]	1%[a]
none	0.80			
2a	0.44	0.45	0.44	0.45
2b	0.45	0.50	0.51	0.52
2c	0.60	0.45	0.49	0.55
2d	0.55	0.51	0.55	0.65
2e	0.43	0.50	0.55	0.64

[a] Concentration of alkylphosphinic acid in PAO-4.

[†] (2-Hexyldecyl)phosphinic acid **2b** is a new compound. Experimental details and NMR spectra of **1a–e** and **2a–e** are provided in the Online Supplementary Materials.

[‡] The purpose of four-ball test is to determine the wear preventive characteristics of a lubricant. In a test, a 12.7 mm steel ball is rotated against three lubricated stationary steel balls under a specified load (196 N in our experiments) with a speed of 1200 rpm within 60 min (ASTM D-4172). The better the lubricant is at preventing wear, the smaller the wear scar is on the three stationary balls. At the end of the test, the three wear scars were measured, and the average value is reported.

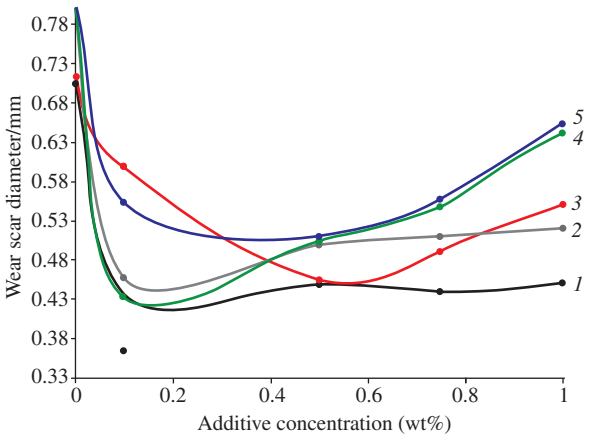


Figure 1 The dependence of anti-wear properties of alkylphosphinic acids *(1)–(5)* **2a–e**, respectively, on the concentration for synthetic PAO-4 oil.

9-methylidenenonadecane was close to acids obtained from lower α-olefin dimers in terms of molar efficiency with a more explicit optimum.

In summary, we evaluated the prospects of using potentially thermally stable branched alkylphosphinic acids, which were prepared from available α-olefin dimers, as organic friction modifiers. Derivatives of linear α-olefins demonstrate good anti-wear properties in hydrocarbon oils. The detailed investigations of these types of OFMs including their thermal stability are underway. The development of a new field of α-olefin dimers utilization will be an expected result of these studies.

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Online Supplementary Materials

Supplementary data associated with this article (description of the synthetic procedures, ^{1}H, ^{13}C and ^{31}P NMR spectra, details of the investigation of anti-wear properties) can be found online at doi: 10.1016/j.mencom. 2019.09.027.

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