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Copolymeric Succinamic Acids as Antiwear Additives: Synergistic and Adverse Effects

Abstract

Copolymeric succinamic acid (COSMA) additives have been synthesised in the laboratory and evaluated for their antiwear performance, both alone and in combination with zinc dialkyldithiophosphate (ZDDP) in HVI light neutral oil. COSMA additives show antiwear behaviour and, in combination with ZDDP, exhibit a good synergistic effect, reducing the wear-scar diameter by 60% and increasing the initial seizure load from 50 kg to 85–95 kg.

Keywords

Antiwear additives, copolymers, succinamic acids, COSMA, synergistic/adverse effects

INTRODUCTION

Lubricants are formulated with different types of additives to provide smooth operation during their use in service. Studies have revealed that additives possessing different functional groups in varying concentrations and combinations when present in multicomponent mixtures affect the individual additive performance and may have synergistic or adverse effects.[1–4] Additive–additive interactions have been reported to have an effect on various characteristics, such as oxidation, detergency–dispersancy, flow improvement, and tribological factors. Synergistic and adverse effects have been observed with combinations of surface active/reactive additives.[1–3, 5–10]

Dicarboxylic acid esters, such as diethyl sebacate, in small additions, are reported to improve considerably the antiwear efficiency of organic sulphides (di-*n*-butyl disulphide, dialkyl disulphide, diphenyl disulphide, dibenzyl disulphide, and dicyclohexyl disulphide). Synergistic and adverse antiwear behaviour of combinations of zinc dialkyldithio-

Table 1 Composition of various synthesised COSMA additives and their antiwear performance in HVI light neutral oil at 1.0 wt.% concentration

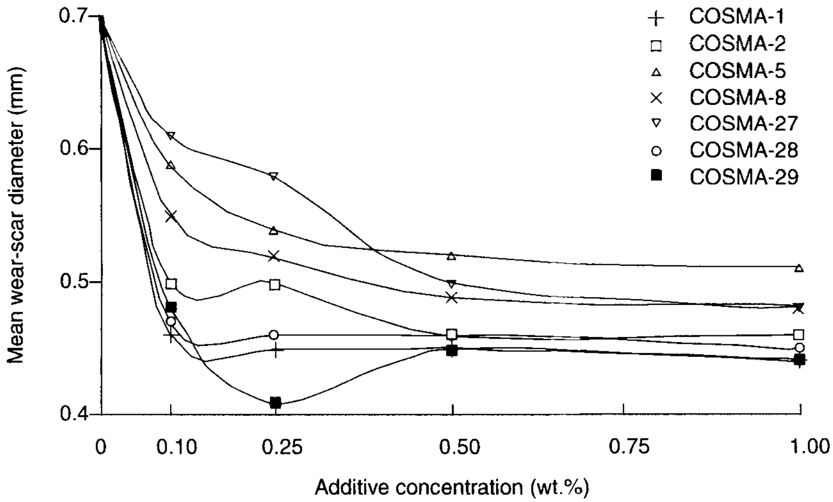
Additive	*Monomer used**	*Amine used*	*Mean WSD at 20 kg load (mm)*
None	–	–	0.70
COSMA-1	LMA and MA	Diethyl	0.44
COSMA-3	LMA, VA, and MA	Diethyl	0.44
COSMA-2	LF and MA	Diethyl	0.46
COSMA-5	LF, VA, and MA	Diethyl	0.51
COSMA-17	CF, VA, and MA	Diethyl	0.50
COSMA-7	LMA[1], LF, VA, and MA	Diethyl	0.44
COSMA-4	LMA[2], LF, VA, and MA	Diethyl	0.46
COSMA-6	LMA[3], LF, VA, and MA	Diethyl	0.44
COSMA-21	LMA, 2EHF, VA, and MA	Diethyl	0.50
COSMA-27	LMA, LM, VA, and MA	Diethyl	0.48
COSMA-16	LMA, CF, VA, and MA	Diethyl	0.49
COSMA-28	LMA, LF, and MA	Diethyl	0.45
COSMA-8	LMA, LF, VA, and MA	Di-*n*-butyl	0.48
COSMA-12	LMA, LF, VA, and MA	Dicyclohexyl	0.53
COSMA-13	LMA, LF, VA, and MA	Morpholine	0.43
COSMA-14	LMA, LF, VA, and MA	Piperidine	0.52
COSMA-29	LMA, LF, and MA	Di-*n*-butyl	0.44

*LMA, lauryl methacrylate; MA, maleic anhydride; VA, vinyl acetate; LF, lauryl fumarate; CF, cetyl fumarate; 2EHF, 2-ethylhexyl fumarate; LM, lauryl maleate; [1–3] ratio of LMA in increasing order.

phosphate (ZDDP), succinimide, alkyl salicylate, sulphonate, and friction-forming polymers and complex esters have also been reported.[4]

The present paper covers the synthesis of 17 copolymeric succinamic acids (COSMAs) of different monomeric ester and

Figure 1 Antiwear performance of COSMA additives in HVI light neutral oil at different concentrations



amine compositions and their antiwear performance, both alone and in combination with a commercial ZDDP additive in mineral base fluids. The evaluations were carried out using a four-ball machine.

EXPERIMENTAL: Synthesis of copolymeric succinamic acid (COSMA) additives

Lauryl methacrylate (LMA) monomer was prepared by the transesterification reaction between methyl methacrylate and lauryl alcohol using an acid catalyst and molecular sieve.[11] The fumaric and maleic esters of 2-ethylhexyl, lauryl, and cetyl alcohols were prepared by the direct esterification reaction between the corresponding acids and alcohols.[12] Monomers, vinyl acetate, and maleic anhydride were procured from commercial sources.

The COSMA additives were prepared by a two-step process.[6] In the first step, interpolymers were prepared by polymerisation of the desired monomer mixture using benzoyl peroxide as a catalyst in benzene solution. In the second step, interpolymers were refluxed with the desired amine in xylene and purified with methanol to give COSMA additives. Monomers and amines used for the synthesis are given in **Table 1**.

Table 2 Antiwear performance of various COSMA additive combinations in HVI light neutral oil*

Additive combination	*Additive concentration (wt.%)*	*Mean WSD at 20 kg load (mm)*
COSMA-1	0.5	0.45
COSMA-2	0.5	0.46
COSMA-1 + COSMA-2	0.25 + 0.25	0.41(+)
COSMA-4	0.5	0.48
COSMA-16	0.5	0.51
COSMA-4 + COSMA-16	0.25 + 0.25	0.43(+)
COSMA-6	0.5	0.47
COSMA-12	0.5	0.54
COSMA-6 + COSMA-12	0.25 + 0.25	0.60(–)
COSMA-8	0.5	0.49
COSMA-29	0.5	0.44
COSMA-8 + COSMA-29	0.25 + 0.25	0.42(+)
COSMA-27	0.5	0.50
COSMA-28	0.5	0.46
COSMA-27 + COSMA-28	0.25 + 0.25	0.41(+)

*(+) Synergistic effect; (–) adverse effect.

Base fluids and evaluation of antiwear characteristics

Three mineral base fluids, HVI light neutral oil, naphthenic refrigeration oil, and liquid paraffin with viscosity around 11–13 cSt at 40°C, were used in the study. The commercial antiwear additive ZDDP (primary) was used in the additive combination study and its concentration was adjusted in terms of Zn content.

The antiwear performance of the blends was determined using a four-ball machine following the IP 239 method. The antiwear performance was assessed on the basis of the reduction in wear-scar diameter (WSD) under 20 kg load and 10 min duration. Each WSD measurement quoted represents three results with an error of 5%. Load-carrying capacity under light load boundary conditions was assessed in terms of the initial seizure load (ISL) for which the test duration was 1 min and the load was applied in steps of 5 kg.

Table 3 Antiwear performance of COSMA additives at 0.25 wt.% and ZDDP at 0.005 wt.% (metal) combinations in HVI light neutral oil*

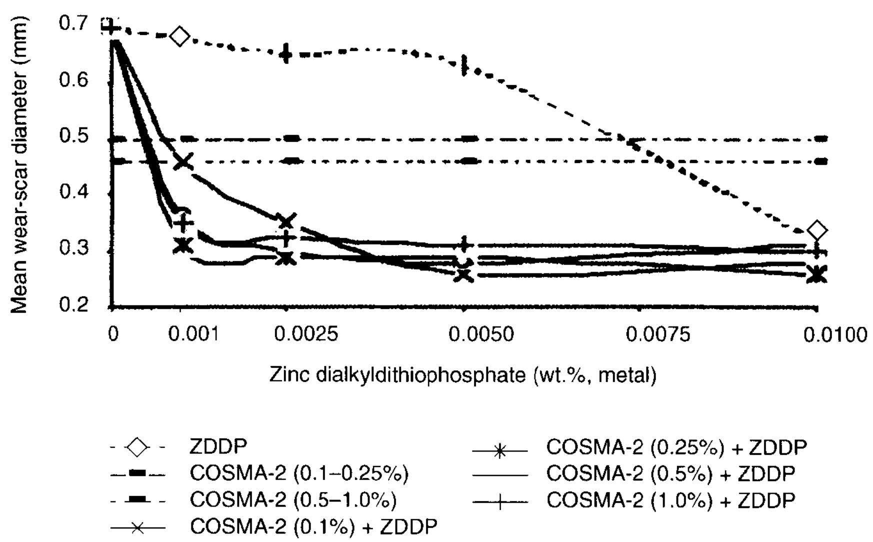
Additive combination	*Mean WSD at 20 kg load (mm)*	
	Without ZDDP	*With ZDDP*
None	0.70	0.63
COSMA-4	0.48	0.29(+)
COSMA-8	0.46	0.28(+)
COSMA-28	0.46	0.30(+)
COSMA-1	0.45	0.29(+)
COSMA-21	0.53	0.28(+)
COSMA-16	0.51	0.28(+)
COSMA-8	0.49	0.30(+)
COSMA-12	0.54	0.27(+)

*(+) Synergistic effect.

RESULTS AND DISCUSSION: Antiwear performance of COSMA additives

The antiwear performance of synthesised COSMA additives in HVI light neutral oil at 1.0% concentration is given in **Table 1**. These additives, in general, reduced the WSD by 24–38% with respect to the base oil. COSMA additives based on LMA were marginally superior to fumarate-based products. Increasing the LMA ratio (COSMA-7, COSMA-4, and COSMA-6) in the copolymeric composition had little effect. COSMA additives having similar monomer composition but with a change in amine nature were found to influence the antiwear performance; products based on diethylamine (COSMA-7) and morpholine (COSMA-13) exhibited a relatively superior performance. **Figure 1** shows the effect of concentration (0.1 to 1.0%) of selected COSMA additives on the antiwear performance in HVI light neutral oil. Additives COSMA-1, COSMA-28, and COSMA-29 showed a steady performance and were effective, even at 0.1% concentration. For the rest of the additives, a decrease in concentration below 0.5% resulted in less of an antiwear effect.

Figure 2 Synergistic effects in the antiwear action of ZDDP and COSMA-2 additive combinations at different concentrations in HVI light neutral oil



Antiwear performance of additive combinations

The effects of COSMA additive combinations were compared, as were those of COSMAs plus the conventional antiwear additive ZDDP. The synergistic/adverse effects of combinations were considered with respect to the antiwear effect produced by the most effective additive component in the combination at the same concentration. **Table 2** gives the antiwear performance of various COSMA additive combinations. It may be observed that additive combinations, in general, exhibited marginal synergistic effects, reducing the WSD by a further 6–10% over that for the more effective single additive. Adverse effects were noticed with the COSMA-12 combination with COSMA-6.

Good synergistic effects were observed with COSMA–ZDDP combinations (0.25% and 0.005%, respectively) (**Table 3**) as the WSD was reduced significantly (57–61%). The antiwear performance of COSMA-2–ZDDP combinations studied with varying concentrations (0.1–1.0% and 0.001–0.01%, respectively) of additives is shown in **Figure 2**. In general, all the combinations exhibited a good synergistic antiwear effect

Table 4 Load-carrying properties of COSMA additives at 1.0 wt.% and ZDDP at 0.005 wt.% (metal) combinations in HVI light neutral oil

Additive combination	*Initial seizure load (kg)*	
	Without ZDDP	*With ZDDP*
None	50	55
COSMA-1	65	85
COSMA-2	60	70
COSMA-27	50	65
COSMA-28	60	75
COSMA-29	55	85
COSMA-4	55	95
COSMA-4 (0.01%)*	55	85
COSMA-4 (0.5%)	55	85
COSMA-4 (2.0%)	55	85

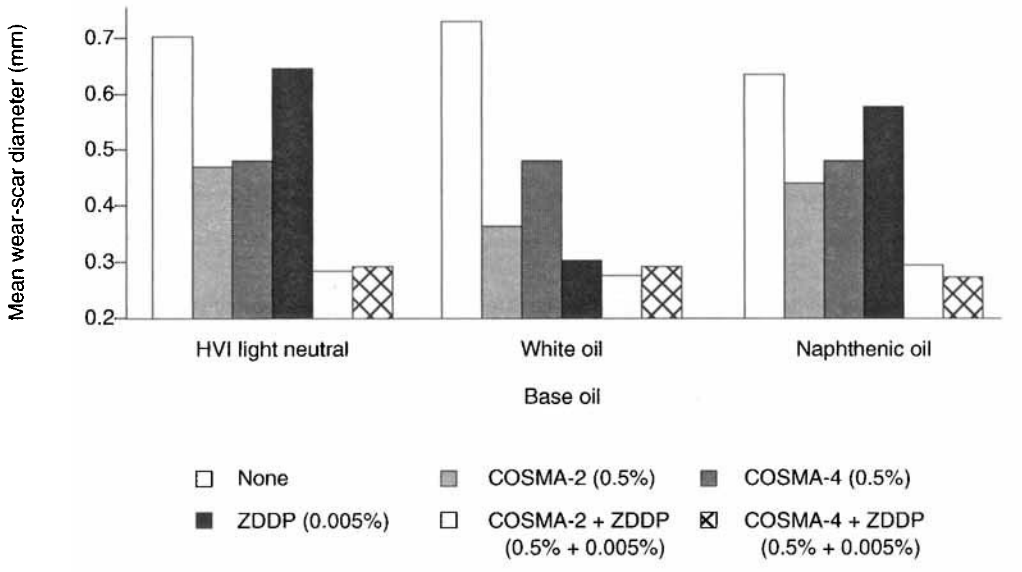
*Concentration of ZDDP is 0.01%.

with the exception of a few at lower concentrations of ZDDP. The reduction in WSD was noticed with increased ZDDP concentration in the combinations. The optimum synergistic effect was observed with COSMA-2 at concentrations of 0.10% and 0.25% plus ZDDP (0.005–0.01%), which reduced the WSD by a further 48% with respect to the most effective component and gave an overall reduction of 63% with respect to the base oil.

Load-carrying performance of COSMA additives and their combinations

The antiwear performance of COSMA additives (1.0%) and their combinations with ZDDP (0.005%) in terms of their load-carrying capacity (ISL) is given in **Table 4**. It is evident that COSMA additives and ZDDP alone effect a marginal increase in the ISL of the base fluid (by 5–10 kg). However, when used in combination (COSMA-1/COSMA-29 and ZDDP), the ISL value increased synergistically from 50 kg to 85 kg, showing an overall improvement of 41%. Data generated with COSMA-4–ZDDP combinations at different concentrations revealed the maximum ISL value of 95 kg with a combination of 1.0% and

Figure 3 Effect of COSMA additive and ZDDP combinations on the antiwear action in different mineral base fluids



0.005% concentration, respectively, showing an overall improvement of 90%. Other combinations of COSMA-4 also resulted in a synergistic effect up to an ISL value of 85 kg.

Role of mineral base fluid

The antiwear effects of COSMA-2 and COSMA-4 additives alone and in combination with ZDDP were investigated in three different hydrocarbon mineral base oils (**Figure 3**). COSMA-2, COSMA-4, and ZDDP alone exhibited a better response in white oil (a paraffinic base fluid) than in the naphthenic refrigeration oil or mixed HVI light neutral oil – the best response was shown by ZDDP. The observation is found to be well in line with the earlier reported work.[8,13] Combinations of COSMA and ZDDP exhibited a synergistic effect in all three base oils; hence the nature of the base fluid has no significant role in the antiwear performance with synergistic combinations. With both the combinations, the WSD was reduced to almost the same level (55–62% reduction).

Under light load boundary conditions, the effectiveness of COSMA additives may be due to a strong adsorption phenomenon through the multiple polar groups present in the ester-based polymers. The antiwear action of ZDDP is known to be caused by decomposition accompanied by oxidation, resulting in the formation of a tenaciously adherent reaction layer on metal surfaces. The strong synergistic effect of COSMA–ZDDP combinations may be the result of the *in situ* formation of reaction products followed by strong adsorption on the moving metal surfaces, a phenomenon similar to that reported earlier with succinimide–ZDDP combinations.[14–16]

CONCLUSIONS

1. COSMA additives show good antiwear performance by reducing the WSD compared to that of the base oil by 24–38%.
2. A strong synergistic effect has been observed with combinations of COSMA additives and ZDDP, reducing the WSD by a further 34–50% with respect to the most effective additive on its own, and giving an overall reduction in the range 57–61% compared with the base oil alone.
3. COSMA additive–ZDDP combinations also exhibit a synergistic response in increasing the ISL of the base oil from 50 kg to 85–95 kg.
4. The synergistic combination has been found to retain the antiwear effect in different base oils.

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