

Occupational allergic contact dermatitis from the extreme pressure (EP) additive zinc, bis ((O,O'-di-2-ethylhexyl) dithiophosphate) in neat oils

Marléne Isaksson, Malin Frick, Birgitta Gruvberger, Ann Pontén and Magnus Bruze

Department of Occupational and Environmental Dermatology, Malmö University Hospital, SE-205 02 Malmö, Sweden

Key words: allergic contact dermatitis; bis ((O, O'-di-2-ethylhexyl) dithiophosphate); CAS 4259-15-8; CAS 68649-42-3; contact allergy; 2-ethylhexyl zincdithiophosphate; extreme pressure (EP) additive; metalworking fluid; neat oil; occupational; zinc.

Neat oils and soluble oils containing 80–90% mineral oil may contain extreme pressure additives (EPAs), which are added to prevent metalworking fluids (MWFs) from being squeezed out from between the tool and the workpiece. These additives are activated by great heat and combine with the metal surface, forming a solid lubricant (1). 1 group of commonly used EPAs are the metal salts of thiophosphoric acid. Among these dithiophosphates, the zinc salts (zinc dithiophosphates, ZDTPs) have found the widest application in the lubricant industry. They also act as antioxidants, corrosion and wear inhibitors and are used in hydraulic oils, greases, and engine and gear oils. The various ZDTPs used in industry differ chemically by the organic group which is bound to the dithiophosphate. These organic groups are alkyl, aryl or cycloalkyl groups.

To date, only 1 article (2) describes a machinist allergic to the EPA zinc, bis ((O,O'-di-2-ethylhexyl) dithiophosphate), a primary dialkyl dithiophosphate, in the aforementioned report. This EPA zinc is also often called 2-ethylhexyl zinc dithi-

ophosphate (EHZDTP) in material safety data sheets (MSDS). We describe another 4 metalworkers with contact allergy to ZDTPs, 3 of the workers participating in a survey of occupational skin disease in 1 of the largest metalworking factories in northern Europe (3) and 1 referred from another smaller metalworking plant because of skin manifestations.

The 3 metalworkers (1 atopic, 2 nonatopic) from the same factory developed work-related hand dermatitis after contact with 2 neat oils (neat oil nos. 1 and 2). Patch testing was performed according to the recommendations of ICDRG. The neat oils provoked allergic patch test reactions and in a 2nd patch test session, the 3 workers were patch tested with components of the 2 neat oils. 1 component, an EPA (EPA no. 1) present at 3.0% in both neat oils, provoked allergic-looking patch test reactions (Table 1). The manufacturer of EPA no. 1 informed us that the substance was zinc, bis ((O,O'-di-2-ethylhexyl) dithiophosphate) (CAS no. 4259-15-8). The MSDSs of the respective oils clearly stated that zinc dialkyl dithiophosphate (ZDDTP) at 3.0% was present in both oils with the CAS number given. 20 control persons were negative on patch testing with EHZDTP 0.6% pet.

The 4th worker (atopic) also developed work-related hand dermatitis after contact with neat oil no. 3 and when patch tested to this oil reacted positively. She was further patch tested to the components of the oil and reacted to another EPA (EPA no. 2, CAS no. 68649-42-3), containing ZDDTPs with primary and secondary alkyl groups (Table 1). EPA no. 2 also contains 20% mineral oil, but the oil is not added to the final product as a diluent but as part of the manufacturing process from the start. The MSDS of neat oil no. 3 also stated that zinc alkyl dithiophosphate was present at a concentration of less than 1.0%, but no CAS number was given. Neat oil no. 3 was tested at 5.0% pet. in 33 controls with negative results.

ZDTPs are common products, their annual production worldwide being approximately 150,000–200,000 tons (personal communication with the manufacturer of EPA

no. 1, 2000). ZDTPs are manufactured by several companies, but in our cases and in the Finnish case the same manufacturer had supplied the ZDTPs. In major textbooks it is stated that zinc alkyl dithiophosphates may be present as EPAs or corrosion inhibitors (4) but apart from the patient in Finland (2), no case histories of contact allergy to ZDTPs have been published. In 1983, Alomar patch tested 230 metalworkers with zinc alkyl dithiophosphate 10.0% o.o. and 3 were positive (5), but he found no clinical relevance (personal communication, 2000).

The manufacturer of EPA no. 1 informed us that the EHZDTP had a high purity (100%), that it was not a sensitizer in the guinea pig maximization test and a weak sensitizer in a Buehler test. When we asked Basketter to run EHZDTP past the computer programme DEREK it came out negative (personal communication, 2000).

As EHZDTP is used worldwide and is a contact sensitizer, we suggest that it is inserted into national and international MWF series at 6.0% w/w in petrolatum.

References

1. De Boer E M, Bruynzeel D P. Occupational dermatitis by metalworking fluids. In: Menné T, Maibach H I (eds.) *Hand Eczema*, 2nd edn. Boca Raton, FL: CRC Press, 2000: 235–250.
2. Kanerva L, Tupasela O, Jolanki R. Occupational allergic contact dermatitis from ethylhexylzinc dithiophosphate and fatty acid polydiethanolamide in cutting fluids. *Contact Dermatitis* 2001; 44: 193–194.
3. Gruvberger B, Isaksson M, Frick M, Pontén A, Bruze M. Occupational dermatoses in a metalworking industry. in press.
4. Nethercott J R, Holness D L. Industrial processes commonly associated with skin disease. In: Adams R M, ed. *Occupational Skin Disease*, 2nd edn. Philadelphia: W B Saunders, 1990: 292–310.
5. Alomar A, Conde-Salazar L, Romaguera C. Occupational dermatoses from cutting oils. *Contact Dermatitis* 1985; 12: 129–138.

Table 1. Results of patch testing with 3 neat oils and 2 EPAs

Test material	Vehicle	Concentration (% wfw)	Test results Patient no.			
			1	2	3	4
Neat oil no. 1	pet.	50	++	+++	++	NT
	pet.	25	++	++	+	NT
	pet.	12.5	+	+	+	NT
	pet.	6.25	+	?+	–	NT
Neat oil no. 2	pet.	50	++	++	++	NT
	pet.	25	++	+	–	NT
	pet.	12.5	+	?+	–	NT
	pet.	6.25	–	–	–	NT
EPA no. 1	pet.	6.0	++	NT	++	NT
	pet.	0.6	++	NT	+	NT
	o.o.	6.0	NT	+	+	NT
	o.o.	0.6	NT	–	–	NT
	o.o.	0.06	NT	–	–	NT
	o.o.	0.006	NT	–	–	NT
	o.o.	0.0006	NT	–	–	NT
Neat oil no. 3	pet.	50	NT	NT	NT	+++
	pet.	5.0	NT	NT	NT	+++
	pet.	0.5	NT	NT	NT	–
	pet.	0.05	NT	NT	NT	–
EPA no. 2	pet.	0.5	NT	NT	NT	+
	pet.	0.05	NT	NT	NT	–

Address:

Marlene Isaksson

Department of Occupational and Environmental Dermatology

Malmö University Hospital

SE-205 02 Malmö

Sweden

Tel: +46 40 337859

Fax: +46 40 336213

e-mail: marlene.isaksson@skane.se