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Director
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Dr. Richard Niemeier,
Director
Division of Standards
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Transfer
National Institute of
Occupational Safety and Health
4676 Columbia Parkway, C-14
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RE: Request for Comments
Occupational Exposure to
Cutting Fluids
55 FR 20637
May 18, 1990

Dear Dr. Niemeier:

Pennzoil Company is a natural resources company engaged in the exploration, production, refining, and marketing of petroleum products, and the mining and sales of sulphur. We thank the National Institute of Occupational Safety and Health (NIOSH) for the oportunity to submit comments on the hazards associated with the occupational exposure to cutting fluids.

Pennzoil has a great interest in cutting fluids since our Penreco division is a manufacturer and distributor of soluble oil bases and sodium petroleum sulfonates. These chemicals are major components of soluble oil bases and an integral part of the product line which we currently market. We believe that the information submitted here will be very valuable to NIOSH in developing prevention and control strategies for related

exposures. Pennzoil's comments will focus on the following three (3) areas: 1) the significant changes over the past two decades in the base oils used to formulate cutting fluids; 2) The American Society for Testing & Materials (ASTM) Committee's efforts to develop a method for estimating the dermal carcinogenicity activity of petroleum fractions used in cutting oils; and 3) Pennzoil's data on acute toxicity of soluble oil bases and petroleum sulfonates in animals.

Cutting Oil Formulations

Soluble oils are manufactured by the blending of a soluble oil base with a refined mineral oil. Typically, 10-20% of a soluble oil base is blended with 80-90% refined mineral oil to produce a soluble oil. The soluble oil may also contain a dye at a concentration of <1% and/or a biocide at <3%. The soluble oil is then mixed with water to produce the end-product cutting oil. Typically, 5% soluble oil is blended with 95% water. Cutting oil bases manufactured by Penreco may contain some or all of the generic components listed in Table 1. Minimum and maximum percentage ranges of each component formulated into

Penreco soluble oil bases are indicated. The percentage of each component found in the end-product cutting oil/water solution is also indicated, assuming a soluble oil containing 20% base and an end-product cutting oil with a 5% soluble oil, 95% water mix.

Table 1

GENERIC FORMULATIONS OF SOLUBLE OIL BASES

GENERIC COMPONENT	MIN/MAX IN BASE	MIN/MAX IN END-PRODUCT
Surfactant	34/65	0.34/0.65
Co-surfactant	16/46	0.16/0.46
Coupling agents	5/20	0.05/0.20
Mineral oil	1/15	4.01/4.15
Water	1/10	95.01/95.10
Defoamer	<1	<0.01
Coloring agents	<1	<0.01
Biocide	<1	<0.01

As can be seen from this table, all components in the end-product soluble cutting oil/water solution are present at less than one percent, except for mineral oil and, of course, water.

Table 2 below lists the exact constituents which are used by Penreco to formulate a soluble oil base. These soluble oil base additives would then be added to a refined mineral oil to make a soluble oil.

Table 2

SPECIFIC COMPONENTS OF SOLUBLE OIL BASES

CHEMICAL	CAS NUMBER	FUNCTION
Sodium petroleum sulfonate*	68608-26-4	Surfactant
Benzenesulfonic acid, mono-C11-C13 branched alkyl derivatives	68608-88-8	Surfactant
Poly (oxy-1,2-ethanediyl, -nonylphenyl)-hydroxy-	9016-45-9	Surfactant
Tall oil fatty acid	8002-26-4	Co-surfactant
Naphthenic acid	1338-24-5	Co-surfactant
Benzenesulfonic acid, dodecyl-, sodium salt	25155-30-0	Co-surfactant
Propylene glycol	57-55-6	Coupling agent
Tripropylene glycol monomethyl ether	25498-49-1	Coupling agent
Tridecanol	112-78-9	Coupling agent
Diethylene glycol	111-46-6	Coupling agent
Butyl carbitol	112-34-5	Coupling agent
Triethanolamine	102-71-6	Rust inhibitor Co-surfactant
Wax blends	8002-74-2	Defoamer
Potassium hydroxide (45%)	1310-58-3	Neutralizer
Benzotriazole, methyl inhibitor	29385-43-1	Corrosion
Poly(oxy-1,2-ethanediyl), -dodecyl-hydroxy-,phospahte inhibitor	39464-66-9	Corrosion
1,3,5-triazine,1,3,5-tri-ethylhexahydro-	7779-27-3	Biocide
4-(2-nitrobutyl)morpholine	2224-44-4	Biocide
4,4'-(2-ethyl-2-nitrotri-methylene)dimorpholine	1854-23-5	Biocide
Water	7732-18-5	Diluent
Dye**	mixture	Coloring agent

*Petroleum sulfonates are oil soluble and are obtained from sulfonic acids which are produced from selected petroleum fractions. The crude sulfonate (RSO_3Na) is obtained at Penreco as by-product

of an oleum sulfonation process used to produce white mineral oils. Impurities such as carbonates and inorganic salts are removed as a sulfonate product is produced.

**Dye mixture may vary. Typical dye is a mixture of 1,4-dialkylamino anthraquinone and Phenol, 2,2'-[(3,3'-dimethyl-{1,1'-biphenyl}-4,4'-diyl)bis(azo)]bis{4-nonyl}, and 2-naphthenol {(phenylazo)phenyl} azo alkyl dervivatives. The hazardous ingredients, along with percentage in dye mixture and CAS number, are xylene (33%) (1330-20-7), C.I. Solvent yellow 107 (28%) (67990-27-6), C.I Solvent Red 164 (23%) (71819-51-7), C.I. Solvent Blue 98 (12%) (74499-36-8), and nonylpenol (4%) (25154-52-3). As previously noted, dyes will be present in the end-product cutting oil at a concentration of <0.01%.

Development of an ASTM Method to Estimate the Dermal Carcinogenic Activity of Petroleum Fractions Used in Cutting Oils

In 1982, the World Health Organization (WHO) summarized the long-term effects on experimental animals of lubricating base oils. Cutting oils were included in this review (WHO, 1982). In this document several straight cutting oils and water-soluble oils were indicated to have tumorigenic potential in rodents. In reviewing these data, one must keep in mind that base lubricating oils contained in cutting oils from this period, 1950s and 60s, did not receive

the degree of treatment that oils today receive, i.e. hydrotreatment and solvent refining. Retrospectively, it is not surprising that many of these cutting oils were able to induce tumors in experimental animals since these base stocks contained higher concentrations of polynuclear aromatic hydrocarbons. Indeed, the WHO summarized that the carcinogenic activity of mineral oils and derived products seems to be related mainly to the presence and concentration of certain polynuclear aromatic hydrocarbons.

Penreco only uses severely hydrotreated or severely solvent refined base oils in the manufacture of soluble oils and bases. The International Agency for Research on Cancer (IARC) has concluded that highly refined mineral oils are Group 3 substances, "not classifiable as to their carcinogenicity to humans", based on inadequate evidence in humans and animals (IARC, 1987). In order to document the degree of treatment severity, Penreco relies on a short-term genotoxicity assay, the modified Ames assay, as a predictor of dermal carcinogenicity in mice. Blackburn et al., (1983, 1986) and Mackerer et al., (1984) have developed a modification of the Ames Salmonella mutagenesis assay which has proven to be a sensitive, reproducible, and cost effective short-term screening method for predicting carcinogenic potencies of mineral oils with median boiling points above 500^{o} F.

In 1988 Roy et al., published a paper which discussed the correlation of mutagenic and dermal carcinogenic activities of mineral oils with polycyclic aromatic content (PAC). In this paper, Roy noted that a significant correlation was observed (> 0.95) between the 3-7 ring polycyclic aromatic compound and both the mutagenic and carcinogenic potencies for samples ranging from those with median boiling points above 500° F. Data were presented which showed that 100% of the carcinogenic oils exhibited more than 1% PAC, while 88% of the noncarcinogenic oils had PAC's content of less than 1%. Roy concluded that the PAC components are largely, if not entirely, responsible for both the carcinogenic and mutagenic activities.

The ASTM E-34.50 Subcommittee on Health and Safety Standards for Metalworking Fluids is concerned about the carcinogenic potential of lubricant oils used in the manufacture of cutting oils. In June, 1988 it was agreed that a task group be formed to address the issue of development of a standard method of estimating the dermal carcinogenic activity of petroleum fractions. After reviewing possible test methods, it was agreed that the modified Ames assay should be the basis for the to-be-developed method. The assay parameters are now being finalized. It is expected than round-robin testing to validate the assay should begin in 1991. If the test is

validated, and there is no reason to believe differently, it should become an ASTM method by 1992. It is emphasized that this assay only has applicability for the virgin base oils used to formulate cutting oils, and not for the blended product containing additives.

The WHO (WHO, 1982) did indicate that in the case of cutting oils, the temperatures to which oils are exposed at the cutting edges of the tools are such that cracking of the oil might conceivably occur, and theoretically, a non-carcinogenic oil might conceivably become carcinogenic during use. In the WHO publication, evidence is provided which shows that used cutting oils are more carcinogenic than virgin cutting oils. If the ASTM method is adopted, it would not be considered reliable for the testing of used cutting oils, which would contain a variety of contaminants besides polynuclear aromatic compounds.

Acute Toxicity of Cutting Oil Bases and Petroleum Sulfonates in Animals

Penreco has tested a series of soluble oil bases and sodium petroleum sulfonates, the principle component of soluble oil bases, for acute dermal and eye irritation using the Draize methods as adopted by the Consumer Product Safety Commission (CPSC).

To test for eye irritation, the method described in 16 CFR 1500.42 was used. To summarize, rabbits were treated with 0.1 ml of test material, and irritation scores were determined at 1, 24, 48, and 72 hours. These scores were used to determine an irritation category

(Kay and Calandra, 1962) and classification CPSC for the test material in nonwashed eyes. For the Penreco soluble oil bases and sodium petroleum sulfonates tested, the maximum irritation scores ranged from 21-31, which correlated to a descriptive rating of moderately irritating. All soluble oil bases were considered irritants by the CPSC classification scheme.

To test for primary irritation of the skin, the method described in 16 CFR 1500.41 was used. To summarize, 0.5 ml test material was applied to one intact and one abraded test site of each rabbit and occluded for 4 hours. The sites were scored for signs of skin irritation at 5, 24, 48, and 72 hours after application. A primary skin irritation index (PII) was determined based on the criteria described in the CPSC method. The soluble oil bases tested had PII's which ranged from 2.5 (mildly irritating) to 4.3 (moderately irritating). The sodium petroleum sulfonates tested had PII's which ranged from 4.0-4.5 (moderately irritating).

Conclusion

We appreciate this opportunity to submit information to NIOSH on the hazards associated with exposures to cutting fluids and hope that this information will assist the agency in developing strategies for preventing and controlling these related exposures.

Yours very truly,

REFERENCES

Blackburn, G. R., Schreiner, C. A., Deitch, R. A. and Mackerer, C. R. (1983). Modification of the Ames Salmonella/microsome assay for testing complex hydrocarbon mixtures. Environ. Mutagen. 5, 466 (abstract).

Blackburn, G. R., Deitch, R. A., Schreiner, C. A. and Mackerer, C. R. (1986). Predicting tumorigenicity of petroleum distillation fractions using a Modified Salmonella Mutagenicity assay. Cell Biol. Toxicol. 2, 63-84.

International Agency for Research on Cancer (IARC) (1987). IARC Monographs on the Evaluation of the Carcinogenic Risk of Chemicals to Humans: Overall Evaluations of Carcinogenicity: An Updating of IARC Monographs Volumes 1 to 42, Supplement 7, pp. 252-259, IARC, Lyon, France.

Kay, J. H. and Calandra, J. C. (1962). Interpretation of eye irritation tests. J. Soc. Cosmetic Chem. 13 (6), 281-289.

Mackerer, C. R., Blackburn, G. R., Deitch, R. A., Dooley, J. F., Schreiner, C. A. and Mehlman, M. A. (1984). Correlation of in vitro Mutagenicity with Dermal Carcinogenicity for Complex Petroleum Derived Mixtures. Presented at the Skin Carcinogenicity Symposium, Centre Henri Becquerel, Rouen, France, June 20, 1984.

Roy, T. A., Johnson, G. R., Blackburn, G. R. and Mackerer, C. R. (1988). Correlation of mutagenic and dermal carcinogenic activities of mineral oils with polycyclic aromatic compound content. Fund. & Appl. Tox., 10, 466-476.

WHO (1982). Selected Petroleum Products, Environmental Health Criteria 20, Geneva, pp. 78-79.