

CHAPTER 16

**Interrelationships Between Biodeterioration, Chemical Breakdown, and Function in Soluble Oil Emulsions**

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Two metalworking fluids, a reclaimed soluble oil and a virgin soluble oil, were examined in an effort to correlate loss of fluid function with degradation of the hydrocarbon by microbial action. Hydrocarbon degradation was monitored by infrared spectrophotometry and gas chromatography, while fluid function was measured by the Falex #8 Tapping Torque machine. Significant hydrocarbon degradation of the C<sub>14</sub>-C<sub>20</sub> series was observed in the presence of aerobic and anaerobic populations in both fluid types. The rate at which degradation occurred was directly related to Ca<sup>++</sup> and Mg<sup>++</sup> in the diluting water, as well as to the complexity of the emulsification systems employed in the fluid concentrates. Statistically, no significant functional differences between intact degraded and undegraded fluids were noted.

INTRODUCTION

Microorganisms have long been associated with deterioration of metalworking fluids (Ellis et al. 1957; Bennett 1972; Heinrichs and Rossmore 1971; Rossmore 1974; Holtzman and Rossmore 1977). Preventing deterioration should increase the useful life of these fluids and thereby increase productivity. Productivity drops when metalworking fluids lose their desired characteristics of performance, resulting in the following: (1) inability to meet surface finish or size tolerances; (2) corrosion of machine tools and work pieces; (3) problems with employees due to offensive microbial odors; and (4) excessive "down time" from having to change fluids and clean systems. The formation of fecal and musty odors, hydrogen sulfide, and ammonia are all common in the industrial environment, and it is important to control their formation to prevent subsequent production losses.

In the past few years, the use of re-refined or reclaimed soluble oils has increased markedly due to the high cost and lack of availability of naphthenic and paraffinic base stocks used in the production of virgin soluble oil concentrates. Because of this general trend, information regarding the susceptibility of reclaimed fluids to microbial attack is needed. Thus, of the two formulations used in this study, one was a re-refined or reclaimed soluble oil (Sol A)

composed essentially of a paraffinic base, with petroleum sulfonate and tall oil fatty acid as the emulsification system (Weintraub, pers. comm.); the other was a virgin formulation (Sol B) with the same base type and emulsification system, with an ester compound for additional lubrication (Parsons, pers. comm.).

The loss of fluid function was measured by a process of metal removal and correlated with a chemical change in the hydrocarbon fraction. Chemical monitoring of the experimental systems was performed using gas chromatography and infrared spectrophotometry. Microbiologically inert controls were evaluated in all systems.

Although several workers (Holodnik and Edwards 1974; Mattison et al. 1975; Skells and Cohen 1977; Hill 1976; Holdom 1977; Sutcliffe et al. 1979) have employed various mechanical methods to evaluate cutting fluid performance, success has been limited. The Falex #8 Tapping Torque machine is the latest approach to standardization of a test procedure to measure the efficiency of a cutting fluid while removing metal (Webb and Holodnik 1980). However, this latter study is limited to straight oils and is yet to be used with water-soluble fluids.

## MATERIALS AND METHODS

### *Biodeterioration Phase*

*Simulated industrial protocol.* A modification of an established laboratory procedure (Heinrichs and Rossmore 1971) was employed. The soluble oils were diluted 1:20 with laboratory tap water containing 450 ppm  $\text{Ca}^{++}$  and  $\text{Mg}^{++}$  (Sol A hard) or the tap water diluted with equal amounts of distilled water (Sol A mod and Sol B mod).

*Microbiological inoculation and monitoring.* A fluid sample from the field with classical signs of biodeterioration (i.e., bluing/darkening of fluid,  $\text{H}_2\text{S}$  production, high aerobic counts, and recoverable sulfate reducers) was used as inoculum. Systems received 10% v/v ( $\sim 100$  ml) of this inoculum.

Enumeration of aerobic bacteria was by the standard plate-count method in Trypticase Soy Agar (TSA)(BBL) incubated at 35 C for 24 h. Sulfate reducers were enumerated semiquantitatively utilizing S-R Deeps (Biosan Laboratories, Inc., Ferndale, MI), incubated at 35 C for 5 d, and examined at daily intervals. The following aerobic species were identified by API 20E (Analytab Products, Division of Ayerst Laboratories, New York, NY) in the inoculum: *Serratia liquefaciens*, *Klebsiella pneumoniae*, *Klebsiella oxytoca*, *Escherichia coli*, *Pseudomonas aeruginosa*, and *Pseudomonas* sp. (fluorescent group).

The total aerobic count of the inoculum was  $2.3 \times 10^3$ /ml, while sulfate reducers were recovered at a level of  $2 \times 10^3$ /ml. Aliquots were removed weekly for both aerobic and anaerobic counts. Aerobic counts were done in TSA.

### *Chemical Monitoring Phase*

*Infrared spectrophotometry.* Samples were monitored on a Beckman 252MX

computing spectrophotometer. Samples were prepared on NaCl discs with spacer to achieve uniform film thickness. Water was removed slowly from the disc surface by heat-lamp evaporation. Scan range was  $4000\text{ cm}^{-1}$  to  $250\text{ cm}^{-1}$  wavenumber at gain setting 050.

*Gas chromatography.* Samples of degraded and undegraded emulsions were analyzed using a Hewlett-Packard 5730A chromatograph (Hewlett-Packard, Palo Alto, CA) equipped with a flame-ionization detector. The column used was a Union Carbide W982 stainless-steel, 3 ft  $\times$  1/8 in., silicon rubber unit. The carrier gas was helium, with an initial column temperature of 80 C and a final temperature of 270 C. A rate of 8 C/min was employed. Detector temperature was 250 C, with injector temperature at 300 C.

*Evaluation of function.* The design and properties of the Falex #8 Tapping Torque machine are given by Faville and Voitik (1978), and the test method has been subsequently described by Webb and Holodnik (1980). The nut blanks used were AISI 1117 steel (Falex #008-500-001), and taps were 10  $\times$  1.5 mm cutting taps (Falex #008-501-001).

## RESULTS AND DISCUSSION

### *Biodeterioration*

The three fluids (Sol A hard, Sol A mod, and Sol B mod) varied in intensity of blackening after 1 wk from inoculation. This apparently was directly related to the degree of anaerobic microbial activity and the water hardness of the systems. Sol A hard had the greatest degree of sulfate reducer activity. The amount of hydrogen sulfide (and subsequently FeS) produced in this system was far greater than that in the other two (Fig. 1).

The microbiological activity in Sol A hard is seen in Fig. 2. The difference in appearance of this fluid prior to inoculation and after 2.5 wk of microbial attack testified to the excessive growth of sulfate reducers in the latter system. The system with Sol A mod with 225 ppm hardness showed less visual anaerobic deterioration. The quantitative microbial results are seen in Fig. 3. Sol B mod was very similar to Sol A mod quantitatively, but visually the reclaimed oil (Sol A) appeared much blacker. The low aerobic counts seen in Figs. 2 and 3 at 6.5 wk may have been due to a 1 wk discontinuance of aeration during a formal corporate holiday. Thus, fluid formulation as well as water quality appeared to contribute to the rate of degradation.

It has been demonstrated (Isenberg and Bennett 1959; Guynes and Bennett 1959) that certain components of cutting fluids are inhibitory to sulfate-reducing bacteria. These compounds include sodium and petroleum sulfonates, sodium resins, and naphthenic acids. Aerobic bacterial populations oxidize these components thereby reducing their inhibition of sulfate reducers. As the latter become active, the characteristic signs of fluid degradation appear. The stimulatory effect of inorganic salts on aerobic bacteria is well documented (Imelik 1948; Bennett 1974). The use of hard water appears to accelerate aerobic activity, therefore oxidizing inhibitory components much more rapidly.

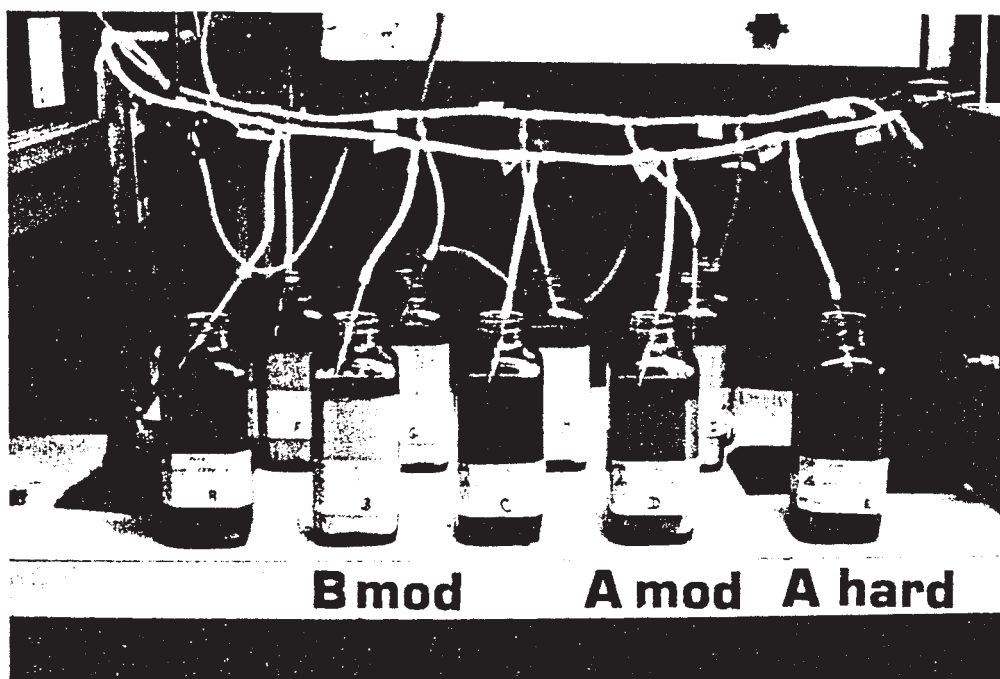


FIG. 1. Simulated industrial protocol showing fluids after 12 wks of maintenance. B mod - virgin soluble oil (Sol B) in 225 ppm ( $\text{Ca}^{++}$  plus  $\text{Mg}^{++}$ ) water. A mod - reclaimed soluble oil (Sol A) in 225 ppm ( $\text{Ca}^{++}$  plus  $\text{Mg}^{++}$ ) water. A hard - reclaimed soluble oil (Sol A hard) in 450 ppm ( $\text{Ca}^{++}$  plus  $\text{Mg}^{++}$ ) water.

The reclaimed fluid (Sol A) seemed to contain a minimal amount of emulsifier. The use of hard water coupled with reduced levels of sulfate-reducer inhibitors resulted in the early appearance of deterioration. The initial count (week 1) for the hard water system was  $10^7/\text{ml}$ , higher by at least 1 log than either of the two systems in moderate water. It appears that greater aerobic activity precedes more intense sulfide production. In the reclaimed system with moderate water (Sol A mod), the initial aerobic count was lower, resulting in less anaerobic activity and therefore formation of fewer anaerobic degradation products. The virgin system (Sol B mod) contained a more complex emulsifier system and moderately hard water and had the least amount of fluid degradation.

#### *Chemical Monitoring*

*Infrared spectrophotometry.* Samples were analyzed prior to inoculation and ~ 12 wks after inoculation. The results indicated a definite loss in the hydrocarbon fraction of the cutting fluid. The spectrum shown in Fig. 4 is that of Sol A before inoculation. The peaks of primary importance are seen at  $2900\text{ cm}^{-1}$ , the main hydrocarbon peak, with the confirming peaks at  $1460\text{ cm}^{-1}$  and  $1380\text{ cm}^{-1}$  due to methylene and methyl banding, respectively. The peak at  $1200\text{ cm}^{-1}$  represents a sulfonate, with the confirming peak at  $1060\text{ cm}^{-1}$ . The peak at  $720\text{ cm}^{-1}$  is an alkane peak (Parsons, pers. comm.).

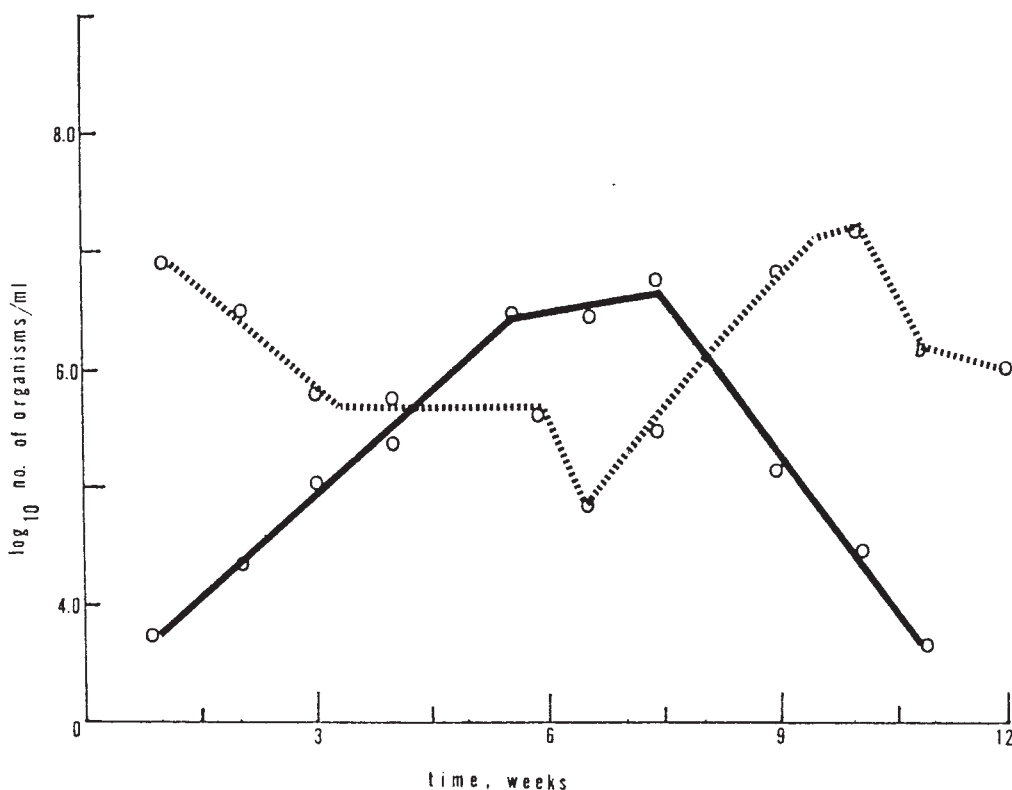


FIG. 2. Growth of aerobic and anaerobic organisms in Sol A hard 5% reclaimed soluble oil (450 ppm  $\text{Ca}^{++}$  plus  $\text{Mg}^{++}$ ). Line = anaerobic organisms; Broken line = aerobic organisms. Points are averages of duplicate colony counts.

Sol A mod, degraded by microbial growth, showed a distinct reduction in the peak at  $2900\text{ cm}^{-1}$ , with corresponding reduction of the confirming peaks at  $1460\text{ cm}^{-1}$  and  $1380\text{ cm}^{-1}$ . The sulfonate peak appeared to be relatively unaffected. A new peak appeared at  $890\text{ cm}^{-1}$ . Although the peak at  $720\text{ cm}^{-1}$  was still present, its intensity was decreased.

In contrasting the spectrum of Sol A hard degraded (Fig. 5) with the previous two, there is a significant reduction in all of the important peak regions. This emulsion was considered unstable and essentially split into two phases at the time of analysis.

The spectrum for Sol B mod control is essentially the same as that for Sol A mod except for the presence of a peak at  $1750\text{ cm}^{-1}$ , representing the ester compound mentioned previously (Parsons, pers. comm.). The confirming peak for this compound should appear at  $\sim 1160\text{ cm}^{-1}$ ; however, it is masked by the sulfonate peak at  $1200\text{ cm}^{-1}$ . The spectrum from Sol B mod with growth is essentially the same as the Sol B mod control except for the disappearance of the ester peak at  $1750\text{ cm}^{-1}$ . It appears that this compound was utilized preferentially by the microorganisms.

The visual biodeterioration seen was confirmed by infrared (IR) analysis. The most visibly altered fluid also exhibited an IR spectrum that indicated greatest loss of hydrocarbons. The second most visually degraded fluid yielded

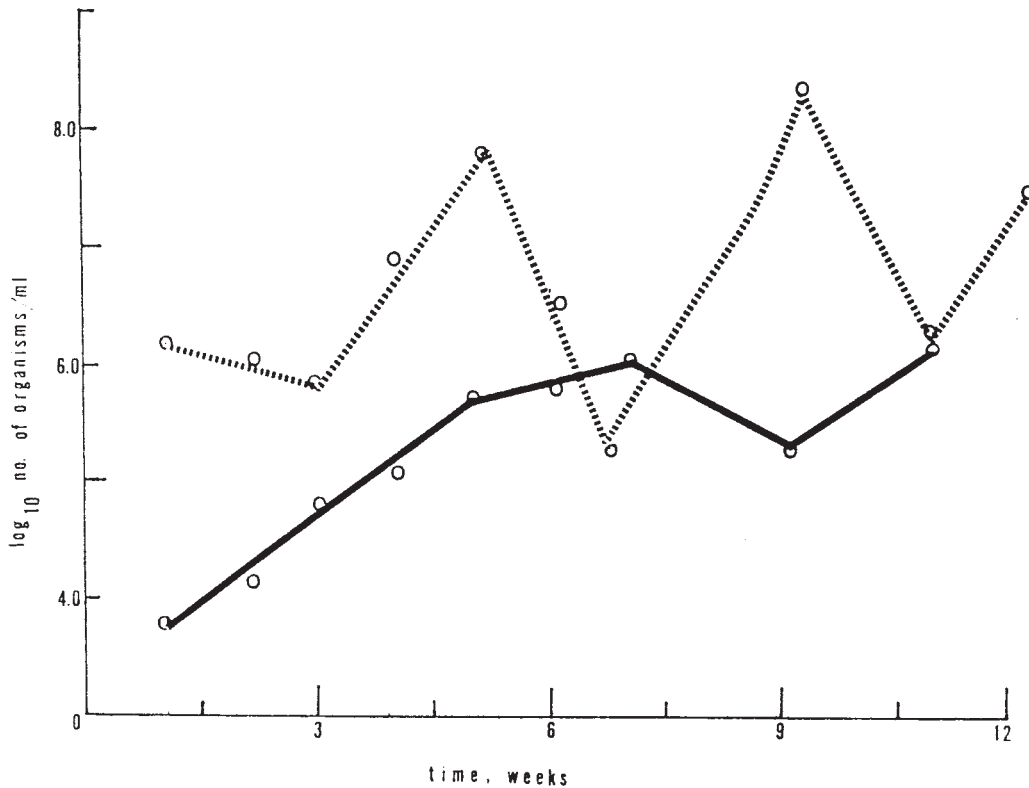


FIG. 3. Growth of aerobic and anaerobic organisms in Sol A mod 5% reclaimed soluble oil (225 ppm  $\text{Ca}^{++}$  plus  $\text{Mg}^{++}$ ). Line = anaerobic organisms; Broken line = aerobic organisms. Points are averages of duplicate colony counts.

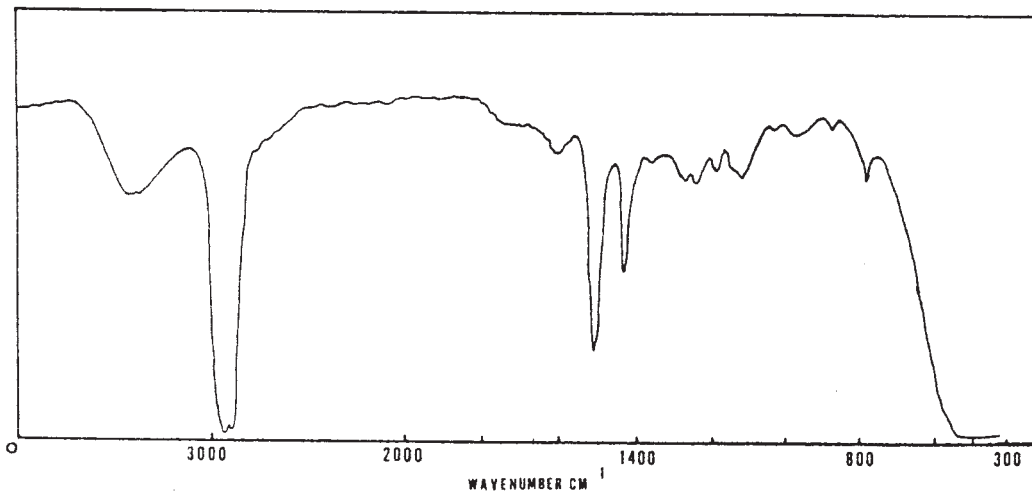


FIG. 4. Infrared scan of 5% reclaimed soluble oil before inoculation.

a spectrum that showed a moderate loss of hydrocarbons, and the spectrum of the least altered fluid showed essentially no hydrocarbon loss; however, there was a preferential destruction of an ester compound.

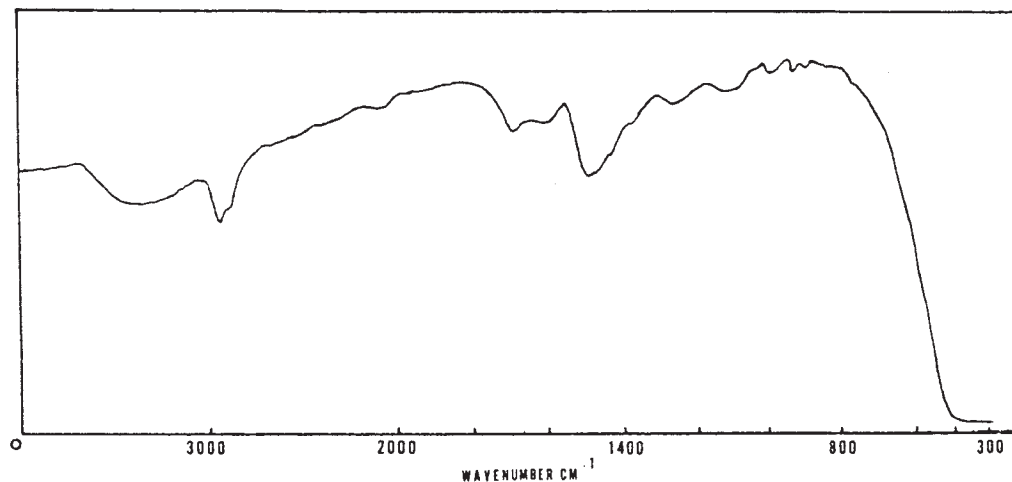


FIG. 5. Infrared scan of Sol A hard 5% reclaimed soluble oil in hard water (450 ppm Ca<sup>++</sup> plus Mg<sup>++</sup>) 12 wks after inoculation.

*Gas chromatography.* The five systems analyzed by IR also were evaluated by gas chromatography. The hydrocarbon C<sub>14</sub>-C<sub>20</sub> series is significantly degraded in both the reclaimed and the virgin fluid. The spectrum for Sol B mod exhibited a configuration considerably different from Sol A mod. Since the exact formulations were not available, the reasons for the spectral differences can only be speculative; however, the hydrocarbon series are discernible with little difficulty. Spectra for reclaimed oil in hard water before inoculation (Fig. 6) and after growth (Fig. 7) show losses in hydrocarbon peaks after growth.

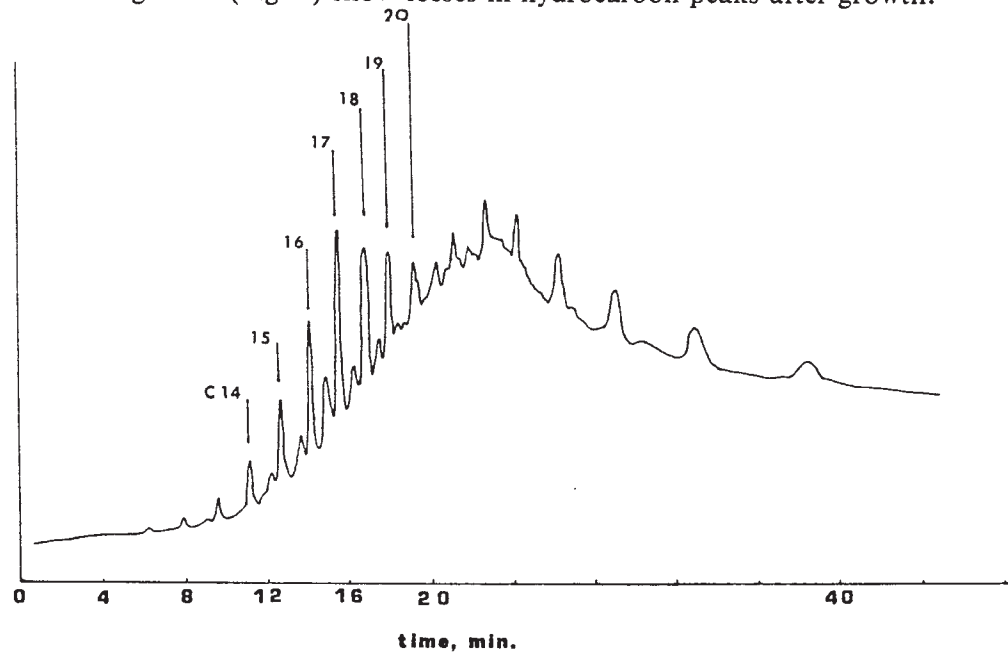


FIG. 6. gas chromatographic scan of 5% reclaimed soluble oil showing hydrocarbon series C<sub>14</sub>-C<sub>20</sub> before inoculation.

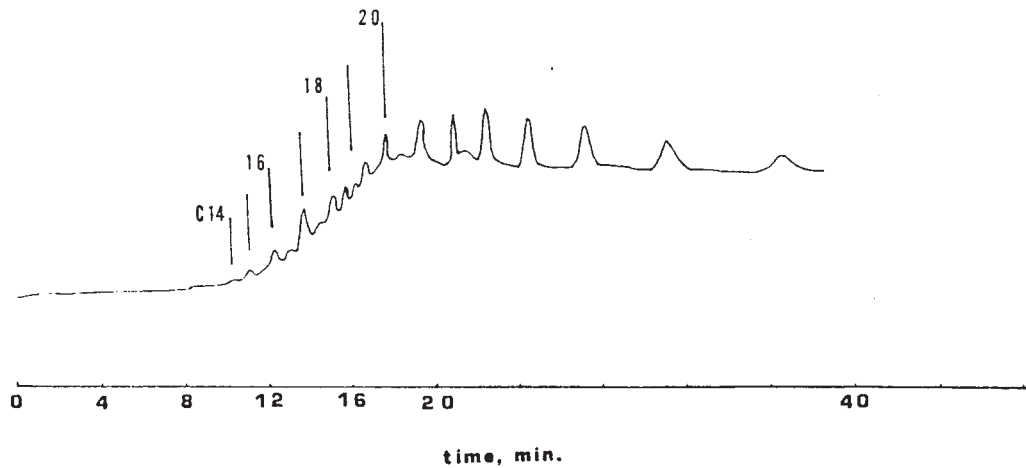


FIG. 7. Gas chromatographic scan of 5% reclaimed soluble oil in hard water (450 ppm  $\text{Ca}^{++}$  plus  $\text{Mg}^{++}$ ) 12 wks after inoculation.

*Function evaluation.* Fluid samples were subjected to Falex testing at Gulf Science and Technology Company, Cheswick, PA. Selected data generated in this phase of the study are summarized in Table 1. The standard deviation as a

TABLE 1. Tapping torque values for cutting AISI 1117 steel determined 12 wk after inoculation of fluids

	Ref Fluid (5%v/v)	Sol A Hard Degraded	Sol A mod Degraded	Sol B mod Degraded
	6.56	6.92	6.34	6.49
	6.20	7.29	6.35	6.51
	6.48	7.16	6.34	6.53
	6.22	7.42	6.19	6.42
	6.46	8.26	6.25	7.03
	6.31	8.28	6.37	6.14
	6.07	6.72	6.78	6.58
	6.82	7.44	6.63	6.42
	6.33	-*	6.58	6.37
	6.12	-	6.41	6.48
	6.18	-	6.96	6.83
	6.23	-	6.27	6.38
Repeatability $\epsilon$ X	75.98	-	77.47	78.16
Mean $\bar{X}$	6.338	-	6.456	6.513
Std Dev Data, S	0.2145	-	0.2336	0.2285
Std Dev Mean, $S_x$	0.0619	-	0.0674	0.0660
95% Conf.Lim., Data	$\pm 0.4720$	-	$\pm 0.5141$	$\pm 0.5030$
95% Conf.Lim., Mean	$\pm 0.1363$	-	$\pm 0.1484$	$\pm 0.1452$
Std Dev as % of Mean	0.98	-	1.04	1.01
% Efficiency	100.00	0.00	98.08	97.21
95% Conf.Lim.	+2.15	-	+2.25	+2.17
*Seizure				

percent of the mean, the percent tapping efficiency, and the 95% confidence limits are found at the bottom of the table. The deviation as a percent of the mean is a measure of the precision of the test. The values indicate good precision and are consistent with standard deviations observed with straight oil testing (Webb and Holodnik 1980) using the Falex #8 machine.

Two types of tests have been employed to measure efficiency of cutting fluid, one type without metal removal (Faville and Faville 1968) and the other with metal removal (Sutcliffe et al. 1979; Skells and Cohen 1977). The former procedure, although useful in measuring sliding friction, cannot duplicate the metal-removal process. The latter procedures are unable to provide reproducible results. Often these tests show standard deviations of 20-40% under laboratory conditions (Webb and Holodnik 1980).

The data generated for these water-extendable fluids, including data for uninoculated systems not presented here, indicate excellent precision and reproducibility, with standard deviation values for all systems lying between 0.76% and 1.75%.

The tapping efficiency and 95% confidence limit values indicate essentially no statistical variation between intact emulsions with and without microbial growth. The failure of the degraded Sol A hard emulsion (Table 1) due to tap seizure indicates that the test procedure can discern between a truly degraded emulsion and an intact fluid; however, its ability to indicate more subtle changes in fluid quality are not evident under the conditions of this test, as illustrated by the overlapping confidence limit values.

#### CONCLUSIONS

This study indicates that the quality of water used as a diluent for oil-in-water emulsions is critical in extending the useful life of a metalworking fluid. The water quality affects the emulsion stability in two ways: (1) the presence of inorganic salts stimulates aerobic growth, thus reducing inhibitory factors that may delay sulfate reducer activity; and (2) emulsion stability is affected by the formation of calcium salts of petroleum sulfonates.

Gas chromatographic analysis and infrared studies indicate a preferential degradation of the C<sub>14</sub>-C<sub>20</sub> series in these formulations.

The characteristic signs of deterioration appear only after anaerobic organisms are found. Aerobic populations degrade hydrocarbons (Ellis et al. 1957; Pivnick 1955; Pivnick et al. 1955; Ladd 1956). The ecological succession and interaction of these organisms is of ongoing interest.

In order to increase fluid longevity, two things must be considered: the use of quality water to maintain fluid stability and antimicrobial compounds to retard the action of microbial populations.

In terms of the functional portion of the study, it is important to recognize that many factors contribute to the performance characteristics of a cutting fluid (e.g., corrosion control, lubrication, cooling, etc.). It appears that the Falex #8 test must be refined so that subtle variations in fluid quality can be detected by measuring torque values.

It should be noted that these results are not inconsistent with field observations where many systems function with aerobic populations  $>10^8$ /ml without

apparent changes in operational efficiency. More often than not, it is the human factor (i.e., unpleasant sights and smells of microbial activity) rather than a breakdown in function that forces remedial action. Perhaps a better method for evaluating fluid function would prevent the production of un-treatable problems.

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#### LITERATURE CITED

- Bennett, E. O. 1972. The biology of metalworking fluids. *Lubr. Eng.* 28:237-247.
- \_\_\_\_\_. 1974. Water quality and coolant life. *Lubr. Eng.* 30:549-555.
- Ellis, L. E., R. S. Maharajah, L. M. Mendelow, L. Ruth, and H. Pivnick. 1957. Oxidation of components of soluble oil. *Appl. Microbiol.* 5:345-348.
- Faville, W. A., and R. M. Voitik. 1978. The Falex Tapping Torque machine. *Lubr. Eng.* 34:193-197.
- Faville, F. A., and W. A. Faville. 1968. Falex procedures for evaluating lubricants. *Lubr. Eng.* 24:349-358.
- Guynes, G. J., and E. O. Bennett. 1959. Bacterial deterioration of emulsion oils. I. Relationship between aerobes and sulfate-reducing bacteria in deterioration. *Appl. Microbiol.* 7:117-121.
- Heinrichs, T. F., and H. W. Rossmoore. 1971. Effects of heat, chemicals, and radiation on cutting fluid flora. *Dev. Ind. Microbiol.* 12:341-345.
- Hill, E. C. 1976. Some aspects of microbial degradation of aluminum rolling coolants. In J. M. Sharpley and A. M. Kaplan eds., *Proc. 3rd Intl. Biodegr. Symp.*, 1975. Applied Science, London.
- Holdom, R. S. 1977. Microbial spoilage of engineering materials. *Tribol. Intl.*:273-280, Oct.
- Holodnik, E., and L. M. Edwards. 1974. Evaluation of cutting fluids with an automatic drilling machine. *Lubr. Eng.* 30:195-200.
- Holtzman, G. H., and H. W. Rossmoore. 1977. Evaluation of action of a formaldehyde condensate germicide. *Dev. Ind. Microbiol.* 18:753-758.
- Imelik, B. 1948. La croissance de *Pseudomonas aeruginosa* sur les petroles. *Comp. Rend.* 226:1227-1228.
- Isenberg, D. L., and E. O. Bennett. 1959. Bacterial deterioration of emulsion oils. II. Nature of the relationship between aerobes and sulfate-reducing bacteria. *Appl. Microbiol.* 7:121-125.
- Ladd, J. N. 1956. Potassium ion stimulation of hydrocarbon oxidation by a soil *Corynebacterium* sp. *Nature* 177:939.
- Mattison, R., G. I. Lloyd, and J. Schofield. 1975. The fatigue effect on En 31 steel balls of microbially degraded soluble oil emulsion. *Tribol. Intl.*:253-255, Dec.
- Pivnick, H. 1955. *Pseudomonas rubescens*, a new species from soluble oil emulsions. *Lubr. Eng.* 70:106.
- Pivnick, H., M. Fuller, H. Graham, and S. Uyeno. 1955. Biological oxidation of soluble oil emulsions. *Lubr. Eng.* 11:96.
- Rossmoore, H. W. 1974. Microbiological causes of cutting fluid deterioration. *Soc. Mfg. Eng. Tech. Paper #MR-169*, 15 p.
- Skells, G. W., and S. C. Cohen. 1977. A drilling test for the evaluation of cutting fluid performance. *Lubr. Eng.* 33:401-406.
- Sutcliffe, T., S. J. Barker, and C. G. Wall. 1979. Coolants — laboratory evaluation by drill test technique using high speed drills. *Lubr. Eng.* 35:145-152.
- Webb, T. H., and E. Holodnik. 1980. Statistical evaluation of the Falex #8 tapping torque test. *Lubr. Eng.* 36:513-529.