Contaminants in used oils and their problems

A Sasaki
KLEENTEK Corporation, 2-7-7 Higashi-Ohi, Shinagawa-ku, Tokyo, Japan

The manuscript was received on 20 May 2005 and was accepted after revision for publication on 14 October 2005.

DOI: 10.1243/135065005X33955

Abstract: Contaminants in hydraulic and lubricating oils are harmful to lubrication. Therefore, contamination control of hydraulic and lubricating oils has been implemented in many factories and oil cleanliness standards of hydraulic and lubricating oils have been established as criteria for oil contamination control. There are two types of oil cleanliness standards: one is based on particle count and the other on gravimetric analysis. NAS 1638, ISO 4406, SAE AS4059, and JISB9930 belong to the former and ASTM D4898 and JISB9931 to the latter. The particle count defines oil cleanliness by counting the number of particulate contaminants in the certain size ranges, and the gravimetric analysis shows the weight of contaminants remaining on a membrane filter disc after a certain quantity of oil was filtered under vacuum, the oil was washed out, and the membrane filter disc was completely dried. Recently, there is a tendency that particle count dominates the technology to judge oil cleanliness. Of course, it is important to quantify the number of particulate contaminants in oils. However, all particles are not contaminants, as particles like graphite and MoS_2, which are countable by particle count, are good additives for lubricants. Therefore, it is very important for us not only to judge oil cleanliness by the particle count but also to know without prejudice what they are. This article discusses some methods to separate contaminants, what contaminants are, and how much they are.

Keywords: contaminants, oil cleanliness standard, particle count, gravimetric method, solvent extraction, oil oxidation products

1 INTRODUCTION

Any oils are contaminated [**1**] and the majority of hydraulic and lubrication problems are attributable to contaminants. As safety and reliability of machinery and components are absolutely important for aerospace industry, Aerospace Industries Association of America, Inc. developed an oil cleanliness standard NAS 1638 titled 'Cleanliness Requirements of Parts Used in Hydraulic Systems', which was made on the basis of SAE ARP 598 (particle count), SAE ARP 743 (particle count of contaminants in air), and SAE ARP 785 (gravimetric procedure) for oil contamination control [**2**, **3**]. NAS 1638 defines oil cleanliness by both particle count and gravimetric analysis. The former counts the number of particulate contaminants in the range of 5–10, 10–25, 25–50, 50–100, and over 100 on a gridded membrane disc, through which oil was filtered, in accordance with the procedure described in SAE ARP 598 and the latter measures the net weight of contaminants on the membrane filter disc by microbalance, as described in SAE ARP 785, after completely removing the oil and solvent. As the rapid development of semiconductor technology needed super-clean environment in order to maintain a high quality of products and a high yield of productivity, automatic particle counters were developed to monitor air cleanliness in clean rooms on real time. The technology of particle count was implemented to oil contamination control and it has almost dominated the contamination control of oils. Although Sir Jost warned in his report of 1965 that poor lubrication had caused substantial losses to industries [**4**], oil changes were the established practice when oils were contaminated. In 1973, OPEC (Organization of Petroleum Exporting Countries) declared oil embargo. In 1970s and 1980s, several researches made in UK reported that 70–85 per cent of hydraulic and lubrication problems were attributable to contaminants in hydraulic and lubricating oils [**5**, **6**]. Since then, many industries started to implement contamination control of hydraulic and lubricating oils. At that time, NAS 1638 was the only one available oil cleanliness standard but it was for aerospace industry. Therefore, ISO 4406 based on particle count was developed for general industries in 1980s. However, both NAS 1638 and ISO 4406 deal particles larger than 4 or 5 μm but do not pay attention to varnish or polymerized oil oxidation products of molecular size. To solve contamination problems of hydraulic and lubricating oils, it is imperative to identify what contaminants are and to investigate what kind contaminants are really harmful to hydraulic and lubricating systems and how they are produced.

2 REVIEW OF THE PAST STUDIES ON CONTAMINANTS

Fitch [**7**] and Hong [**8**] developed and established their contamination control theory [**7**, **8**] and defined contaminants in reference [**7**]. A part of the definition is shown subsequently.

As material contaminants:

(a) a gas, liquid, or solid;
(b) free, dissolved, emulsified, or entrained;
(c) inert, catalytic, or reactive;
(d) organic or inorganic;
(e) deformable or rigid;
(f) inanimate or living;
(g) decomposed, deteriorated, or degraded products.

As energy contaminants:

(a) thermal;
(b) mechanical;
(c) chemical;
(d) electrical;
(e) magnetic;
(f) radiant.

The aforementioned definition gave a good guidance to investigate contaminants but did not specify what the real contaminants in working machinery were. Thus, contamination control has been discussed on the basis of particle count, without defining what contaminants are. For scientific studies, it is very important to verify any test data by third party. Therefore, artificial contaminants like air cleaner fine test dusts, which were available to anyone, were used for tests of hydraulic components [**9**]. On the basis of such tests, some theories claim that the particles equal to or slightly larger than the component's dynamic film thickness are harmful to lubrication and that particulate contaminants smaller than the clearance of moving parts cause little damage [**10**], although maintenance technicians and workers know that varnish of molecular size causes serious damages to lubrication.

Godfrey [**11**] outlined contaminants and tests for amount of contamination. Hamer *et al.* [**12**] demonstrated that not only solid and hard particles but also soft contaminants would damage bearings. Ioannides and Jacobson [**13**] and Ioannides *et al.* [**14**] have worked to quantify the relation of particulate contaminants (material, size, shape, hardness, number) and bearing lives. Snyder *et al.* [**15**] and Le Pera *et al.* [**16**] have demonstrated that particulate contamination was sensitivity of hydraulic components and that chemical products would cause servovalve stuck. Snyder's group took the first step to investigate the properties of harmful contaminants.

3 SEPARATION OF CONTAMINANTS FROM THE USED OILS

Whenever failed hydraulic components are examined carefully, some brown-coloured deposits are seen thereon. Some of extreme examples are shown in Figs 1 and 2. The brown-coloured deposits on the valve shown in Fig. 1 are not solid particles. Then the question is what they are. Particle count can tell us the number of particulate contaminants but not what their properties are. Therefore, it is important to find some methods to separate contaminants in order to know what they are.

Fig. 1 Deposits on a hydraulic valve

Fig. 2 Deposits on a suction strainer

Table 1 The dipole moment of solvents [**18**]

Solvent	Dipole moment (Debye)
n-hexane	0.0
Toluene	0.37 (gas)
Pyridine	2.15

The majority of oils used in industries are made of mineral base oils [**17**]. Oils are chemical products. The molecules of the base oil are non-polar. When they are used in machinery, a part of the oil molecules will oxidize. The oil oxidation products have polarity. Polar materials and non-polar materials are not compatible to each other. In consideration of the property of base oil and that of oil oxidation products, the author has separated the elements of contaminants from the working mineral oils using solvent extraction methods. The dipole moment (the unit is Debye) of the solvents, which are used for the solvent extraction, is shown in Table 1 [**18**].

At first, the contaminated oil will be diluted with *n*-hexane (non-polar solvent). Then they will be separated into two fractions of the *n*-hexane soluble and the *n*-hexane insoluble. Base oils and additives soluble in the base oils will be soluble in *n*-hexane but polar materials and solid particles will not be soluble in *n*-hexane. Therefore, the *n*-hexane insoluble fraction can be counted as the total amount of contaminants. At the next stage, the dried *n*-hexane insoluble part will be washed with toluene. Then, they will be separated into two parts of the *n*-hexane soluble and the *n*-hexane insoluble. The extracted 'toluene soluble fraction' is resinous matter or oil oxidation products. An example of IR spectra of oil oxidation products is shown in Fig. 3. It has a strong peak of absorption at around 1700 cm^{-1}, indicating existence of C=O of —COOH group which is typical to carboxylic acid [**19**]. One of the examples of molecular weight distribution of polymerized oil oxidation products, which were extracted from the oil used for 1 year, is shown in Fig. 4 [**20**]. The separated and dried toluene insoluble part will be dissolved into pyridine. Then, the pyridine soluble fraction will be extracted from the toluene insoluble. The pyridine soluble fraction will be some kinds of metal salts or decomposed materials of additives. The remaining pyridine insoluble part will be worn metals and dust coming from the atmosphere [**21**]. An example of solvent extraction methods is shown in Fig. 5. The solvent extraction methods can separate the oil contamination from the oil and divide into three parts: the first part is oil oxidation products, the second one is decomposed materials of oil additives, and the third one, worn metals and dust. Then the next question will be which is the most of the three. Machines, the maintenance records of which were well kept, were selected and the oil samples were taken from them. Contaminants were separated from the oils by solvent extraction methods. The summary of the results is shown in Table 2. It shows that oil oxidation products are the most of the three in the working oils.

4 CHARACTERISTICS OF OIL OXIDATION PRODUCTS

The results of solvent extraction summarized in Table 2 show that the majority of the contaminants in the working oils were polymerized oil oxidation products of molecular sizes. Polar materials and non-polar materials are not compatible basically. Therefore, oil oxidation products will primarily form dimer by offsetting the dipole charges of the polar groups and will pretend to be non-polar in order to co-exist with non-polar base oil, when they

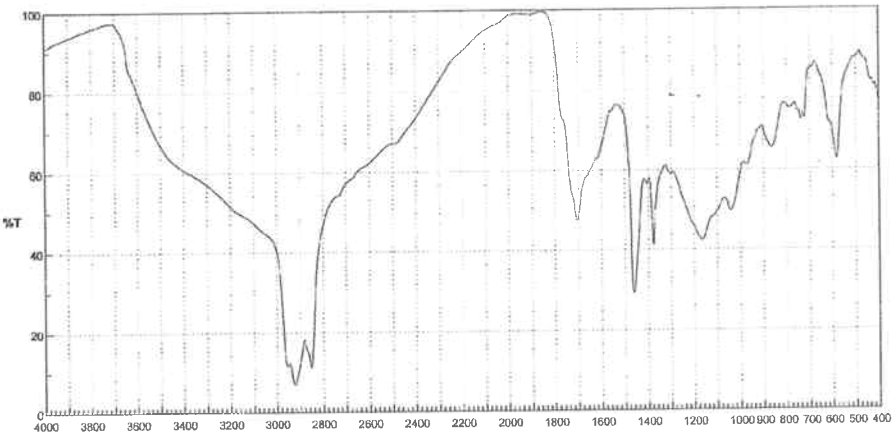

Fig. 3 An example of IR spectrum of oil oxidation products

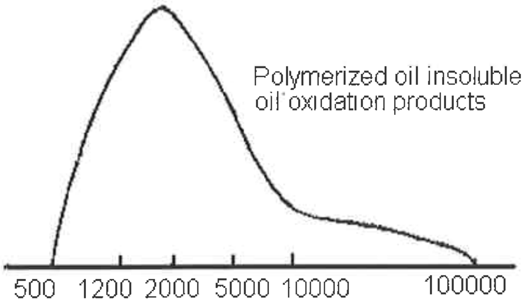

Fig. 4 An example of molecular weight of polymerized oil oxidation products

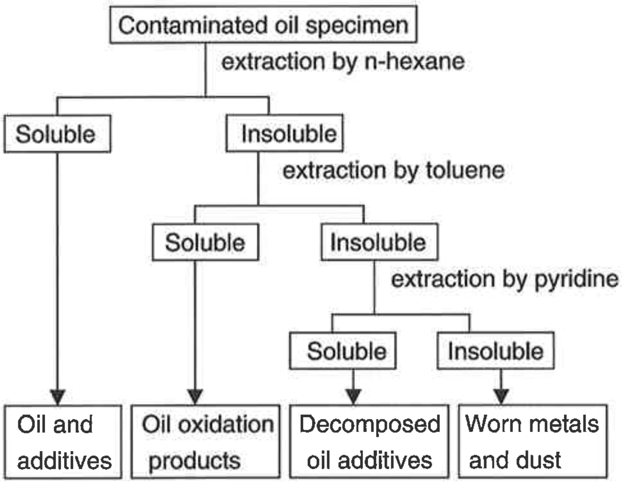

Fig. 5 An example of solvent extraction methods

are formed in oils. As the number of them increases, they will have more chances to come near to the metal surfaces by thermal motion of oil molecules and be adsorbed there. The more in number, the more they will be adsorbed on the metal surfaces from the oil phase. In order to maintain stable conditions, some natural force will work to reduce the total free energy or the total surface energy in a given phase [**22**]. When particles are suspended in oil, the electrical double layer will be created at the side of oil at the interface between a particle and oil. The thickness ($1/\kappa$) of the electrical double layer is given by the following Poisson–Boltzmann equation [**23**]

$$\left(\frac{1}{\kappa}\right)^2 = \frac{\varepsilon KT}{8\pi n z^2 e^2} \qquad \cdots\cdots \qquad (1)$$

where $1/\kappa$ is the thickness of electrical double layer (Debye length: cm), ε the dielectric constant of oil, K the Boltzmann constant, T the absolute temperature, e the electric charge of electron, n the concentration of ion, and z the valence of ion.

As oils are non-conductive, the concentration (n) of ion is very small. Therefore, the thickness of the electrical double layer of the oil is large from equation (1). This means that it is difficult for particles to agglomerate in oil. Then, in order to reduce the total surface of contaminants, when the number of them increases, contaminants will build up deposits on metal surfaces, where permanent dipole moment is large, as shown in Figs 1 and 6. The interaction energy between polar groups is as large as 15 kcal/mol and that between polar group and metal is as large as 13 kcal/mol, although that of the methyl groups is only as large as 0.1 kcal/mol [**24**]. Therefore, polar molecules build up layers on the metal surfaces as shown in Fig. 6 [**24**]. Electrostatic oil cleaners can remove any kinds and sizes of contaminants in oil by electrostatic force [**25**]. When the concentration of oil oxidation products and other contaminants in oil becomes less and less, the deposits will be separated layer-by-layer at the interface where the methyl groups are facing with very low interaction energy, and will go back into oil. If this mechanism is used, it is possible to remove the deposits of polymerized oil oxidation products to the extent that only the first layer remains on the metal surfaces.

5 PROBLEMS OF OIL OXIDATION PRODUCTS

The author oxidized paraffin base oil by RBOT apparatus without adding water and catalysts for 3 h. Then, he measured the molecular weight by Gel Permeation Chromatography and found that three

Table 2 Chemical compositions of contaminants in used hydraulic oils separated by solvent extraction methods

	Sample number				
	1	2	3	4	5
Unit	mg/ml (%)	mg/ml (%)	mg (%)	mg (%)	mg (%)
n-Hexane insoluble	15.3/200 (100)	13.6/100 (100)	84.8 (100)	37 (100)	30.1 (100)
Toluene soluble fraction	7.2 (47)	9.2 (67.6)	52.8 (62.3)	25 (67.6)	22.4 (74.4)
Pyridine soluble fraction	6.3 (41.2)	3.6 (26.5)	25.9 (30.5)	9.7 (26.2)	6.2 (74.4)
Pyridine insoluble	1.8 (11.8)	0.8 (5.9)	6.1 (7.2)	2.3 (6.2)	1.5 (5.0)
Oil age (year)	2	3	3	3	4

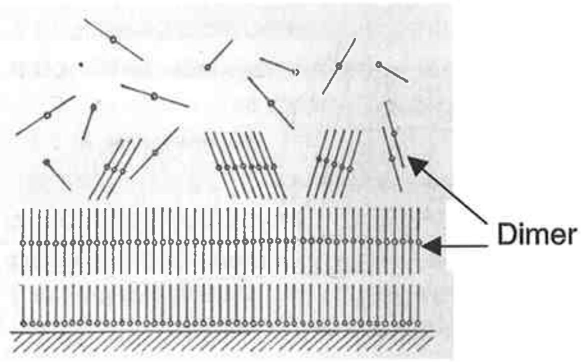

Fig. 6 Schematic figure of forming layers of polar molecules (From reference [**24**])

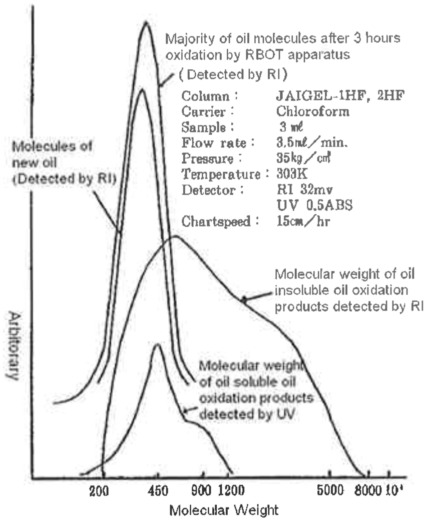

Fig. 7 Three groups of molecules in the oil oxidized by RBOT apparatus for 3 h

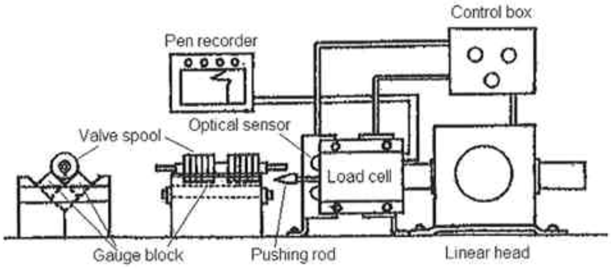

Fig. 8 Friction coefficient measuring machine

groups of molecules existed in the oxidized oil, as shown in Fig. 7. Friction coefficient of the following oils was measured using a friction measurement machine shown in Fig. 8. A pushing rod mounted on a linear head was used to push the valve spool. The operating speed of the linear head was 10 mm/s for the measurement. The friction coefficient was measured at a room temperature of about 25 °C, using a load cell with the maximum load of 0.49 N. The friction coefficient was recorded by a pen recorder.

1. New paraffin base oil (ISO VG 32 $\mathrm{mm^2/s}$).
2. The same paraffin oil was oxidized by RBOT apparatus for 3 h and had three groups of molecules as shown in Fig. 7.
3. The same paraffin oil was oxidized and the oil insoluble fraction was removed.

The friction coefficient of the paraffin new oil was constant regardless of measuring conditions as shown in Fig. 9 but that of the paraffin oil, which was oxidized by RBOT apparatus and had the molecules mixture of three groups as shown in Fig. 7, became substantially high as shown in Fig. 10 when a slider was rested over 5 h. It was because the molecules on the gauge blocks and a slider drew each other by van der Waals force and glued the slider on the gauge blocks, while a slider rested, and because a large force was required to cut the glue. The friction coefficient of the oil, from which the oil insoluble fraction was removed, was low and constant regardless of the measuring conditions, as shown in Fig. 11. It was because there were only two groups of molecules having the peaks at 450 and 900 in molecular weight and because the molecules having the peak at 900 in molecular weight made a uniform and smooth layer at the real contact points and governed the friction [**21**, **26**]. The test results indicate that the oil having oil insoluble oil oxidation products produces high friction coefficient and that it causes hydraulic valve sticking [**21**, **26**]. The problems of polymerized oil oxidation products are not limited to hydraulic valves. The life of filters will be shortened as shown in Fig. 2, and bearings and pumps will fail as shown in Figs 12 and 13.

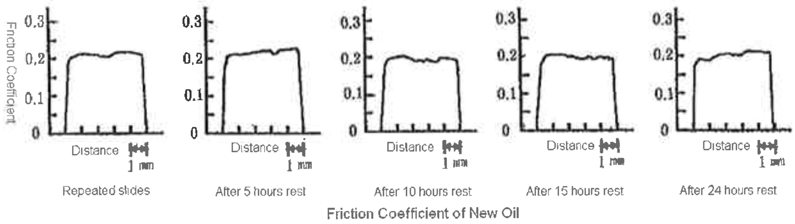

Fig. 9 Measurement of friction coefficient of new base oil

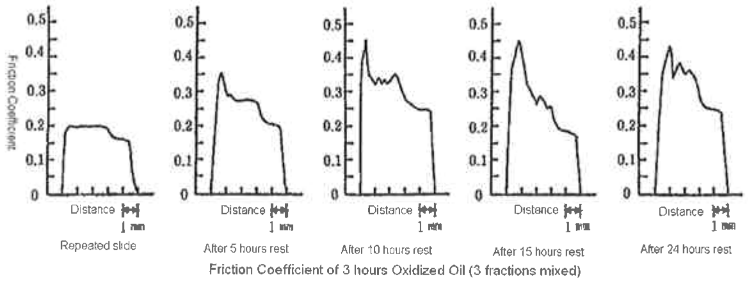

Fig. 10 Measurement of friction coefficient of oxidized oil (three fractions mixed)

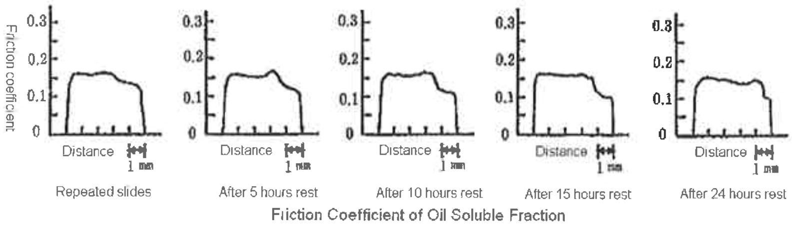

Fig. 11 Measurement of friction coefficient of the oil having the oil soluble fraction and the base oil only

6 HOW ARE THE OIL OXIDATION PRODUCTS PRODUCED?

It is well known by Arrhenius equation that oil oxidation speed becomes almost double at every 10 °C. Almost all hydraulic and lubricating systems incorporate mechanical filters on the main stream of oil, where the velocity of oil flow is very fast. Some systems use a filter on a by-pass loop. When oil passes through mechanical filters, static electricity will be generated. The higher the oil flow velocity, the more the generation of electrostatic charges, the more often the sparks discharges of static electricity happen. Although it has been known among specialists of electrostatics and oils that static electricity is generated when oil passes through narrow passages and filter media and that spark discharges of static electricity happen in filter media and in oil tanks with filters, filter makers have not accepted the facts until recently [**27**]. However, it had been completely overlooked, until the author pointed out, that spark discharges of static electricity, which would be generated when oil passed through mechanical filter, would have damaged oil [**28**, **29**]. When static electricity is discharged with sparks, the temperature is higher than 10 000 K [**30**]. No materials can stand such high temperature. The high temperature cracks oil molecules and produces free radicals. Then, the produced free radical $R^\bullet$ leads to auto-oxidation as shown subsequently [**31**]

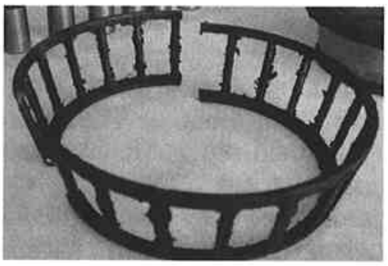

Fig. 12 Failed bearing retainer

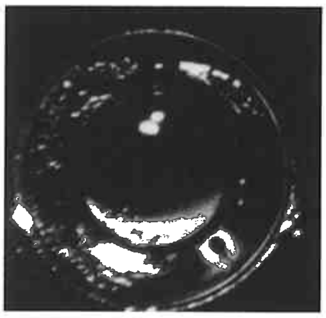

Fig. 13 Pump stuck by varnish

Initiation

$$RH \longrightarrow R^\bullet + H \quad .... \tag{2}$$

Auto-oxidation

$$R^\bullet + O_2 \longrightarrow ROO \quad .... \tag{3}$$

$$ROO + RH \longrightarrow ROOH + R^\bullet \quad .... \tag{4}$$

The free radical $R^\bullet$ reacts with oxygen in oil and becomes peroxi-radical. The peroxi-radical extracts hydrogen from the hydrocarbon of the base oil and reproduces a new free radical $R^\bullet$. The reactions of equations (2) and (3) will repeat even at room temperature in dark [**29**]. Therefore, the reactions between (2) and (3) are called as chain reactions or auto-oxidation. Oil oxidation products will be finally polymerized and become varnish.

This suggests that the root causes of oil damage and of varnish production exist in the current designs of oil circulation for hydraulic and lubrication systems.

7 SUMMARY

1. In the past, the theme of what contaminants are has not been studied.
2. Contaminants were separated from used oils by solvent extraction methods and quantified by weight. It was found that the majority of contaminants were polymerized oil oxidation products, which were soluble in toluene, and that the least were particulate contaminants, which were countable by particle count.
3. Oil oxidation products have polarity and are adsorbed on the metal surfaces, which have permanent dipole moment, to build up deposits.
4. Polymerized oil oxidation products cause high friction to lead lubrication problems.
5. Almost all hydraulic and lubricating oil systems use mechanical filter. When oil passes through filter media, static electricity will be generated. Such static electricity will be discharges with sparks. The temperature of sparks is higher than 10 000 K and the oil can be damaged by the high temperature.
6. The root causes of oil damage and of varnish production exist in the current designs of oil circulation systems.

REFERENCES

1 **Corless, J. R.** Contamination control during the repair of hydraulic machinery. *Contamination Control in Hydraulic Systems Conference*, University of Bath, England, 5–6 September 1984, Paper C240/84, pp. 1–7.

2 *NAS 1638, Oil cleanliness standard*, 1964 (Aerospace Industries Association of America, Inc., Washington).

3 *SAE ARP 598, 743, and 785, Aerospace recommended practice*, 1960, 1962 and 1964 (Society of Automotive Engineers, Inc.).

4 **Jost, P.** Save this country £515 million per annum. *Sci. Lubr.*, 1966, **18**(3), 13.

5 **Spencer, J. B.** and **Balmer, C.** *Effective contamination control in power system*, 1977 (Sperry Vickers Publication, UK).

6 **Day, M. J.** The characteristics of practical systems. *Contamination Control in Hydraulic Systems Conference*, University of Bath, England, 5–6 September 1984, Paper C255/84, pp. 9–23.

7 **Fitch, E. C.** *Fluid contamination control*, 1988 (FES, Inc. Siltwater, OK).

8 **Hong, I. T.** The beta prime – a new advanced filtration theory. *Contamination Control in Hydraulic Systems Conference*, University of Bath, England, 5–6 September 1984, Paper C250/84, pp. 83–88.

9 **Saunders, D. H.** The effect of practical operation conditions on the performance of hydraulic filters. *Contamination Control in Hydraulic Systems Conference*, University of Bath, England, 5–6 September, 1984, Paper C247/84, pp. 101–110.

10 **Pavlat, M. R.** Total cleanliness control for hydraulic and lubricating systems in the primary metal industry. *Lubr. Eng.*, 1997, **53**(2), 12–19.

11 **Godfrey, D.** Clean, dry, oil prolongs life of lubricated machines. *Lubr. Eng.*, 1989, **45**(1), 4–8.

12 **Hamer, J. C., Sayles, R. S.**, and **Ioannides, E.** Particle deformation and counterface damage when relatively soft particles are squashed between hard anvils. *Tribol. Trans*, 1989, **32**(3), 281–288.

13 **Ioannides, E.** and **Jacobson, B.** Dirty lubricants – reduced bearing life. *SKF Bearing J., Special Issue*, 1989, 22–27.

14 **Ioannides, E., Beghini, E., Jacobson, B, Bergling, G.**, and **Goodall Wuttkowski, J.** Cleanliness and its importance to bearing performance. *Lubr. Eng.*, 1993, **49**(9), 657–663.

15 **Snyder, C. E., Gschwender, L. J.**, and **Pellerin, C. J.** Determination of the sensitivity of U.S. air force aircraft hydraulic system components to particulate contamination. *Lubr. Engr.*, 1983, **39**(7), 450–457.

16 **Le Pera, M. E., Messina, J., Mullinger, H.**, and **Snyder, C. E.** Investigation of the causes of stuck servovalves in U.S. army hydraulic system using MIL-H-46170 'Hydraulic Fluid, Rust Inhibited, Fire Resistant, Synthetic Hydrocarbon Base'. *Lubr. Eng.*, 1978, **34**(7), 375–380.

17 **Bock, W.** Hydraulic fluids – a design element – preconditions and possibilities for long-life lubrication. Proceedings of the 49th National Conference on Fluid Power, March 19–21, 2002, Paper no. NCFP102-1.7/SAE OH2002-01-1384, pp. 33–41.

18 *Dictionary of science and technology* (Ed. Tokyo Science University), 1996, pp. 1646–1647 (Nikkan Kyogyo Newspaper (Business & Technology)).

19 **Horiguchi, H.** *Comprehensive survey of infrared spectra (in Japanese)*, Chapter 17, 1977, pp. 195–215 (Sankyo Publishing, Tokyo).

20 **Sasaki, A., Tobisu, T., Uchiyama, S.**, and **Kawasaki, M.** GPC analysis of oil insoluble oxidation products of mineral oil. *Lubr. Eng.*, 1991, **47**(7), 525–527.

21 **Sasaki, A.** *Study of sticking mechanism of hydraulic valves by oil oxidation products.* PhD thesis, Tokyo University of Agriculture & Technology, Chapter 2, 22–51, 1992.

22 **Fermi, E.** Thermodynamics (Translated into Japanese by M. Kato). *Sanseido*, 1988, 81.

23 **Kitahara, F.** and **Watanabe, A.** *Electrical phenomena at interface* (in Japanese), Chapter 6, 1978, pp. 117–140 (Kyoritsu Publishing, Tokyo).

24 **Akhmatov, A. S.** *Molecular physics of boundary friction*, 1963, pp. 212 and 283 (Russia; transl. N. Kaner, Israel, 1964) (The Israel Program for Scientific Translations).

25 **Sasaki, A.** and **Uchiyama, S.** A new technology for oil management: electrostatic oil cleaner. Proceeding of IFPE 2002, Paper No. NCFP 102-1.2/SAE OH 2002-01-1352, pp. 9–18, NFPA, WI, USA.

26 **Sasaki, A.** Hydraulic valve problems caused by oil oxidation products, Hydraulic Failure Analysis: Fluids, Components, and System Effects, ASTM STP 1339, 2001, pp. 474–488.

27 **Duchowski, J., Bensch, L., Phair, B., Khazan, M.,** and **Tsalyuk, V.** Overcoming electrostatic discharge in hydraulic and lubricating applications by incorporating a novel filter media. *IFPE 2005*, Paper no. NCFP105-19.1, 2005, pp. 733–741 (National Fluid Power Association).

28 **Sasaki, A., Uchiyama, S.,** and **Yamamoto, T.** Generation of static electricity during oil filtration. *Lubr. Eng.*, 1999, **55**(9), 14–21.

29 **Sasaki, A., Uchiyama, S.,** and **Yamamoto, T.** Free radicals and oil auto-oxidation due to spark discharges of static electricity. *Lubr. Eng.*, 1999, **55**(9), 14–21.

30 **Murooka, Y.** *Corona phenomena (in Japanese)*, 1989, pp. 41 and 152 (Corona Publishing Co., Tokyo).

31 **Waters, W. A.** The direct oxidation of C–H bond. *Mechanisms of oxidation of organic compounds*, 1964, pp. 6–16 (Methuen, London).