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MAZIVA, MATERIJALI I INŽENJERSTVO PODMAZIVANJA

Sažetak

Prošlo stoljeće i kraj tisućljeća obilježeno je bogatim razvitkom tehnike, tehnologije, materijala i maziva. Međutim, zadnje godine prošlog stoljeća pokazale su da nije samo napredak u tehnologiji i ekonomski razvitak od društvenog značaja, nego i očuvanje okoliša i zdravlje ljudi. Štednja energije i prirodnih izvora postala je središnja briga za očuvanje okoliša. Povećana je briga javnosti za maziva zbog toga što svake godine 40-50% od oko 5 milijuna tona rabljenog maziva završava u okolišu a ne reciklira se nekom od metoda.

Cilj je razviti tribološke sustave, manje štetne za okoliš koji će istovremeno imati i visoka radna svojstva. To je moguće ostvariti primjenom novih materijala ili prevlaka na dodirnim površinama ili primjenom maziva manje štetnih za okoliš i zdravlje s visokim radnim svojstvima. Osim toga kompjutorizacija i razvitak numeričkih metoda, koji su alat za dizajniranje tribološkog sustava te bogata baza podataka i nove metode održavanja i ispitivanja jamče bolju primjenu.

Uvod

Središnja komponenta tribološkog sustava je mazivo čija je najznačajnija funkcija smanjenje trenja i trošenja koji se javljaju pri dodiru dviju površina u relativnom gibanju. Kao podsustav tribološki sustavi integrirani su svuda u tehničke sustave. Osim važnih primjena u motorima s unutrašnjim izgaranjem, zupčaničkim prijenosima i hidrauličkim sustavima, postoji i velik broj daljnjih primjena. Zbog loše izvedbe tribološkog sustava ili neodgovarajuće primjene, ako nije prilagođen za dotični sustav, može doći do komercijalnih gubitaka koji se mjere u bilijunima eura godišnje. Zbog toga značaj tribosustava nije samo u tehničkom smislu nego i u ekonomskom i ekološkom. Koncept budućeg uspješnog razvitka pokušava povezati ekonomiju i ekologiju u cjelovit neproturječan sustav. Napredak tehnike i inovativna istraživanja to omogućuju i to je osnova za intenzifiranje ekoloških aspekata u budućim tehničkim subjektima. Putovi razvitka podmazivanja u prošlom stoljeću, temeljenih na razvitku znanstvenih disciplina i u ovisnosti o potrebama industrije i opreme, prikazani su na slici 1.

Slika 1: Sažetak razvitka podmazivanja u dvadesetom stoljeću

Figure 1: Summary of the lubrication development during 20th century

Prepoznavanjem funkcije tribološkog sustava i bogatim razvitkom materijala, opreme i metoda činilo se da su svi problemi uz podmazivanje riješeni. Međutim, inženjerstvo podmazivanja i dalje ostaje aktivno. Cilj je razviti tribološke sustave, manje štetne za okoliš koji će istovremeno imati i visoke tehničke performance.

Razvitak tehničkih proizvoda ovisan je o nizu općenitih i specifičnih zahtjeva. Općeniti su zahtjevi: kompatibilnost (ekološka), visoka tehnička radna svojstva, efikasnost primjene maziva, konstrukcije i materijala te cijena maziva odnosno ekonomičnost.

Specifični zahtjevi su: smanjenje potrebe za tekućinama/mazivima - kompenzacija materijalima, primjena prirodnih ili kemijski modificiranih prirodnih sirovina, proizvodnja maziva sa smanjenim troškovima, korištenje baza podataka ili numeričkih metoda, štednja energije i prirodnih resursa. Ekonomičnost maziva nije samo njegova nabavna cijena već je to rezultat ocjenjivanja cijelog niza svojstava. To su kompatibilnost (višefunkcijska maziva), starenje i temperaturna stabilnost, interval izmjene ulja, mogućnost recikliranja, troškovi zbrinjavanja, mjere održavanja, investicija u stroj a također i procjenjivanje troškova rada, troškova skladištenja, mjere kontrole emisije, mjere očuvanja zdravlja i sigurnosti pri radu, jednostavnija procedura za dobivanje dopuštenja za primjenu te smanjenje troškova za rješavanje uljnih zagađenja i čišćenja.

Formulacija maziva u novom tisućljeću

Tekuća ili konvencionalna maziva se općenito sastoje od baznog ulja i to najčešće oko 90 % i aditiva oko 10 %. Bazno ulje može biti mineralnog porijekla, sintetičko ili prirodno (biljno i životinjsko).

Tablica 1: Vrste baznih ulja prema API klasifikaciji i osnovna svojstva

Table 1: API Classification of base oils and basic properties

API GRUPA	Zasićeni ugljikovodici, %	Sumpor,%	Indeks viskoznosti
GRUPA I, solventna-rafinacija	ispod 90	> 0,03	80 – 120
GRUPA II, hidroprerada	> / = 90	< / = 0,03	80 – 120
GRUPA III, duboka hidroprerada / izomerizirani parafin	> / = 90	< / = 0,03	120 +
GRUPA IV, polialfaolefini (PAO) polimerizacija, hidrogenacija	definirana formula R-$CHCH_3$-/CH_2-CHR/$_x$-H	-	130 +
GRUPA V	⇒ Sva druga bazna ulja (uključujući i sintetička)		

Tijekom zadnjih dvadesetak godina kakvoća mineralnih baznih ulja se znatno promijenila. Prvi razlog je što su se promijenili izvori nafte a drugi je briga o zaštiti okoliša i zdravlje ljudi. Prije su imala više aromata i smatralo se da su kancerogena. Kakvoća se popravila solventnom rafinacijom i hidrotretiranjem te razvitkom novih postupaka sinteze. Treći razlog poboljšanja kakvoće ulja je u pojačanim zahtjevima za funkcijskim svojstvima maziva, primjerice motornih ulja, kao što su bolja oksidacijska stabilnost, svojstva tečenja, viskoznost i sl. U tablici 1 prikazane su vrste i osnovna svojstva baznih ulja prema API (American Petroleum Institute) klasifikaciji.

Visoki radni zahtjevi za maziva doveli su do sve češće primjene sintetičkih baznih ulja kao što su polialfaolefini, esteri i dr. U tablici 2 prikazana su svojstva sintetičkih ulja u usporedbi s mineralnim uljem.

Tablici 2: Usporedba svojstava sintetičkih i mineralnih ulja

Table 2: Performance of synthetic lubicants compared to mineral oils

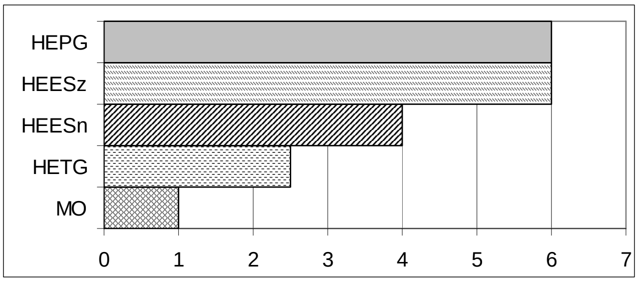
SVOJSTVA/ ZAHTJEVI	Mineralno ulje	Sintetička ulja						
		Sintet. ugljikovodici			Organski esteri			
	parafinsko	PAO	PIB	DAB	DAE	POE	PG	PhE
Interval viskoznosti	širok	jako širok	jako širok	nizak	nizak	nizak	jako širok	nizak
Viskoznost/ovisnost o temperaturi	2	4	3	2	3	3	5	1
Niske temperature	1	4	2	3	3	3	4	2
Visoko temp. stabil. s inhibitorom	2	4	3	3	3	5	3	2
Kompatibilnost s min. uljem	5	5	5	5	3	2	1	1
Niska isparivost	2	5	3	3	5	5	3	3
Kompatibilnost s bojama/lakovima	5	5	5	5	2	2	3	1
Hidrolitička stabilnost	5	5	5	5	2	2	4	2
Stabilnost na smicanje	5	5	3	5	5	5	5	5
Svojstva podmazivanja	2	4	2	2	3	3	4/5	5
Antikorozivna svojstva s inhibitorima	5	5	5	5	3	3	3	2
Stabilnost aditiva	5	3	3	5	4	4	2	3
Kompatibilnost NBR	5	5	3	5	2	2	3	2

*(PAO = polialfaolefin, PIB = poliizobutilen, DAB = dialkilbenzen, DAE = ester dikiseline, POE = poliolester, PG = poliglikol, PhE = fosfatester, NBR= acrilonitril-butadien guma)
**(5=izvrsno, 4=vrlo dobro, 3=dobro, 2=zadovoljavajuće, 1=loše)

U ekstremnim radnim uvjetima, primjerice klimatskim uvjetima-hladnoća, moguća je primjena polialfaolefina. PAO se najviše i upotrebljavaju i to u svim područjima: u industriji, avio industriji, u mastima, hidrauličkim tekućinama, zupčaničkim uljima i dr. Kod primjene PIB i alkilaromata vidljiva su neka ograničenja ali imaju važnu ulogu kao dodaci baznom ulju. Sintetička maziva preporučuju se uvijek tamo gdje osiguravaju pozitivnu bilancu troškova bez obzira na visoku cijenu sirovine. Na slici 2 prikazan je faktor koštanja na primjeru hidrauličke tekućine ovisno o vrsti baznog ulja: HEPG – poliglikoli, HEES - z zasićeni esteri, HEES - n nezasićeni esteri, HETG – biljno ulje (trigliceridi), MO- mineralno ulje.

Slika 2: Faktor koštanja hidrauličke tekućine ovisno o vrsti baznog ulja

Figure 2: Cost factors of hydraulic fluid based on base oil type



Utjecaj zakonskih akata i preporuka raznih udruženja na maziva

Prilikom formuliranja modernih maziva mora se voditi računa o utjecaju pojedinih komponenti na čovjeka i okoliš. Djelovanje maziva na zdravlje i okoliš definirano je sljedećim svojstvima: toksičnost, biorazgradljivost, inhibicija (mikrobna) i bioakumulacija. Utjecaji su regulirani različitim zakonskim normama ili preporukama s obvezatnom primjenom pojedinih država ili grupe država, raznih udruženja te potrošača. Osim različitih zakona i preporuka koji ipak vremenski ne mogu slijediti sve brži razvoj znanosti, proizvođači maziva trebaju kontinuirano pratiti nove spoznaje i tendencije u procjeni toksičnog djelovanja pojedinih tvari. Osobito je to važno pratiti u području tekućina za obradbu metala jer čovjek na radnom mjestu dolazi s njima u izravni dodir, prvenstveno rukama dok poslužuje stroj, zatim rasprskavanjem te udisanjem. Briga o toksičnosti pojedinih komponenti koje se primjenjuju za formuliranje maziva definirana je maksimalno dopuštenim koncentracijama (MDK) u proizvodu, u radnom okolišu (atmosferi) ili u otpadu (kada se ispuštaju u vodotok ili zrak). To je dovelo do razvitka novih grana tehnike a to su: medicina rada, ekotehnika i procesna tehnika. Vrste ispitivanja djelovanja maziva na okoliš i ljude sve se više proširuju i postaju sve sofisticiranije, ali i skuplje. U tablici 3 dan je pregled nekih od obvezatnih ispitivanja, slijed uvođenja i procjena troškova ispitivanja (u tisućama eura). U sigurnosno tehnički list koji je obvezatan za svako mazivo ugrađena su svojstva vezana uz zdravlje ljudi i okoliš, opasnosti, sprječavanje kontakta, prvu pomoć, transportna svojstva i dr.

Tablica 3. Sigurnosni zahtjevi za ispitivanja maziva

Table 3: Safety requirements for lubricants examination

				…	386000€
				teratogenost	
				…	
				mutagenost	
				toksičnost/kinetička	
				…	
		…	42000€	toksičnost/alge	
		Bioakumulacija		Bioakumulacija	
		Osjetljivost		Osjetljivost	
		toksičnost/dermalna		toksičnost/dermalna	
….	8000 €	Daphnie/bakterije		Daphnie/bakterije	
iritacija		iritacija		iritacija	
toksičnost/oralna		toksičnost/oralna		toksičnost/oralna	
toksičnost/ribe		toksičnost/ribe		toksičnost/ribe	
biorazgradljivost		biorazgradljivost		biorazgradljivost	
ispitivanje	trošak	ispitivanje	trošak	ispitivanje	trošak
JUČER		DANAS		SUTRA	

Značajan je utjecaj njemačkog zakona o odgovornosti prema okolišu od 1991. koji je između ostaloga, uveo načelop uzročnika, obvezu informiranja te obvezu poduzimanja mjera opreza i mjere za popravak izvornih uvjeta. Zakonom o otpadu od 1996., koji je integrirao dio zakona o recikliranju, uvedena je obveza da su proizvođači maziva dužni prihvatiti rabljena motorna i zupčanička ulja od potrošača. Proizvođači maziva najčešće uzimaju ovlaštene servise za skupljanje ulja. Troškove skupljanja, rješavanja ili recikliranja obično plaćaju potrošači maziva (između 100 i 200 E/t).

Nadalje, zakonodavac je definirao više kategorija otpada prema sadržaju klora (0,2 %) i PCB koje se moraju zbrinuti propisanim načinom što znatno poskupljuje rješavanje otpada. Visoki troškovi zbrinjavanja otpada vode razvitku i primjeni biorazgradljivih maziva, maziva bez klora ili drugih štetnih spojeva.

Maziva manje štetna za okoliš

Što se događa s mazivima nakon završetka radnog vijeka? Procjenjuje se da svake godine nastaje oko 5 milijuna tona rabljenog maziva. Najveći dio se skuplja kao otpadno ulje 47 %, gubitak maziva u cirkulacijskim sustavima 28 %, regeneracija ili rješavanje na mjestu nastanka otpadnog ulja 11 %, potpuno ili djelomično spaljivanje u motorima s unutrašnjim izgaranjem 6 % i 8 % je total loss podmazivanje. Vidljivo je da se 58 % zbrinjava a 42 % se gubi u okoliš odnosno oko 2 mil t maziva zagađuje okoliš.

To je razlog za pojačan razvitak maziva manje štetnih za okoliš (Environmentally adapted lubricants, EAL). Takva maziva smanjit će troškove zbrinjavanja, troškove za zaštitu voda, održavanje, međufazno čišćenje rekondicioniranje vode iza cijepanja i dr. Isto tako EAL su obično netoksična a imaju i bolju kompatibilnost s kožom. Svojstva maziva prilagođenih okolišu su:

- brza biološka razgradljivost
- niski stupanj zagađenja voda
- slaba topljivost u vodi
- neštetnost ili niska toksičnost
- aditivi bez teških metala
- nezapaljivost/visoko plamište, vodene tekućine
- niska isparivost-visoko plamište
- primjena prirodnih sirovina- esterska ulja, repica, sojino ulje, životinjska ulja

Maziva manje štetna za okoliš primjenjuju se na mjestima gdje se potpuno gube u okoliš, tzv. total-loss podmazivanje. To su pokretni hidraulički sustavi, maziva za skretnice željeznice, pile, sredstva za odvajanje kalupa pri betoniranju i dr. Primjenjuju se i u industriji i to hidraulička, industrijska zupčanička ulja i sl. U formulacijama EAL maziva od aditiva valja izbjegavati spojeve na osnovi olova, klora, barija i cinka (kao ZDDP). Umjesto njih primjenjuju se esteri fosfatne kiseline, alkilen karbamati, spojevi na osnovi “zelenog” bizmuta i drugi spojevi koji nisu štetni. Kao bazno ulje mogu se koristiti sintetički esteri, poliglikoli i neke druge sintetičke bazne komponente.

Najpoželjnija je primjena prirodnih ulja koji mogu dati dobra svojstva mazivu kao aditivi i kao bazna ulja. Prilikom primjene uočene su bitne promjene aktivnosti sintetičkih i prirodnih komponenti u odnosu na formulacije s mineralnim uljem. Stoga su pojačana ispitivanja a prvenstveno se ocjenjuju oksidacijska i temperaturna stabilnost te kompatibilnost aditiva i bazne uljne komponente. Nadalje se ocjenjuje njihova polarnost, aktivnost prema površini, kemijska reaktivnost, svojstvo mogućnosti stvaranja mazivog filma, čvrstoća filma, kapacitet nošenja opterećenja, prijenos topline, ovisnost viskoznosti o temperaturi i dr.

Hidraulička ulja

Potrošnja hidrauličkih tekućina u Njemačkoj u 1995. godini bila je približno 160 000 t. Na osnovu raspodjele potrošnje po tipu procjenjuje se da će do 2005. godine doći do povećanja potrošnje maziva na osnovi mineralnog ulja u stacionarnim sustavima a past će u pokretnim sustavima (tablica 4). Paralelno, u mobilnim sustavima povećat će se potrošnja brzo biološki razgradljivih tekućina, dok će druga ostati na istom stupnju potrošnje.

Tablica 4: Potrošnja i budući razvoj hidrauličkih tekućina (Njemačka, 1995)

Table 4: Hydraulic fluid consumption and development (Germany, 1995)

1995.	Tip hidrulične tekućine	2005.
84 %	na osnovi mineralnog ulja (HLP, HLPD, HD)	? stacionarni ↗
4 %	brzo biološki razgradljiva (HETG, HEES, HEPG)	? mobilni ↗ stacionarni ↘
7 %	vatrootporna (HFC, HFA, HFDU)	7 % jednako
5 %	druga (PAO, HC)	5 % jednako

Povećane su aktivnosti oko specificiranja brzo biološki razgradljivih maziva. Ona moraju zadovoljiti stroge tehničke i ekološke zahtjeve: od specifikacija proizvođača opreme, primjerice Caterpillar, Rexroth, Sauer Sundstrand do zakona i preporuka različitih udruženja u pojedinim državama. Značajni su:

- njemački “Blue Angel”, RAL UZ 79 (brzo biološki razgradljiva hidraulička ulja)
- VDMA Liste 24568, 24589 (VDMA, Udruženje njemačkih proizvođača opreme i postrojenja)

- izvješće njemačkog Ministarstva za hranu, poljoprivredu i šumarstvo
- ISO predspecifikacije ISO L 6743-4 (ISO CD 15380)
- švedski DIN "Gothenburg Paper"
- engleski "Environmental Agency"
- kanadski " Canadian Environmental Choice Program"
- nizozemski " More environmentally friendly lubricants" i dr.
- Europska unija još nema uvedena maziva u svoju direktivu EU 880/92.

Hidrauličke tekućine budućnosti ili brzo biološki razgradljive hidrauličke tekućine moraju zadovoljiti uz ekološke kriterije i tehničke kriterije a sažetak je prikazan u tablici 5.

Tablica 5: Hidrauličke tekućine budućnosti

Table 5: Future hydraulic fluids

VDMA Sheet 24568	"Blue Angel" znak okoliša, RAL UZ 79
Tip: HETG, HEES, HEPG	brzo biorazgradljiva hidraulička tekućina - RBHF
naglasak na tehnička svojstva:	naglasak na ekološke kriterije:
- ponašanje pri niskim temperaturama	- nema spojeva koji zahtijevaju specijalno označivanje
- stabilnost prema starenju	- eko-toksikološki kriteriji
- kompatibilnost s brtvenim materijalima	- stupanj zagađenja vode, WPC
- hidrolitička stabilnost	- bološki razgradljiva
- Linde test, suhi TOST	- tehnička svojstva u skladu s VDMA 24568

Mazive masti

Mineralno ulje je i dalje dominantno bazno ulje za mazive masti. Sve više razvijaju se na osnovi sintetičkih ulja zbog boljih svojstava u odnosu na mineralna ulja kao što su oksidacijska stabilnost, tecivost pri niskim temperaturama, visokotemperaturna svojstva, kompatibilnost s plastikom, vodljivost i dr. Sintetičke masti imaju i nekoliko slabosti. Primjerice silikonsko ulje ima bolji temperaturni raspon viskoznosti ali je loše pri graničnom podmazivanju čelika. Polifenileter ima visoku cijenu i slaba niskotemperaturna svojstva. Za primjenu su bolji diesteri, poliolesteri, polialfaolefini, alkildifenil esteri i dr. Izbor baznog ulja za proizvodnju masti ovisi o zahtjevima primjene a za biološki razgradljive primjenjuju se esteri. U mastima budućnosti od aditiva treba izbjegavati: Pb, Cl, Ba, Zn (kao ZDDP) spojeve. U sustavu ugušćivača mogu se primijeniti "funkcionalni polimeri"

(0,5%) koji imaju funkciju poboljšivača adhezije/kohezije, otpornosti na vodu, sapunske strukture ili drugih svojstava.

Zupčanička ulja

Proizvođači vozila glavni su pokretači razvitka ulja za prijenosnike u vozilima. Glavni ciljevi ocjenjuju se ekonomičnošću potrošnje goriva, produljenjem intervala zamjene ulja, produljenjem radnog vijeka opreme te smanjenjem troškova održavanja.

Trend za novi milenij – utrka proizvođača vozila: poboljšana aerodinamičnost, veće brzine, manji broj okretaja, veća okretna snaga te veće serije. Radni vijek za ulja za automobile najmanje je 100 000 km, a za teška vozila 800 000 km. Zahtijeva se rad u širokom temperaturnom intervalu za što valja poboljšati reološka svojstva maziva. Ovo su zadaci koje moraju riješiti proizvođači opreme OEM (Original Equipment Manufacturer) i proizvođači maziva odnosno aditiva. Postavljaju se zahtjevi za sastav maziva: aditivi na osnovi sumpora i fosfora (S-P aditivi) ili bora (B) uz dodatak poboljšivača indeksa viskoznosti (VII) i antioksidansa. Zupčanička ulja mogu biti jednogradacijska i višegradacijska mineralne osnove, polusintetička ili sintetička.

Testiranje je značajan faktor za zupčanička ulja i provodi se u tri stupnja. Prva su ispitivanja u laboratoriju standardnim metodama (ASTM, DIN) te ispitivanja na “radnim stolovima” i posebnim metodama (dinamičko-mehanički testovi za određivanje čvrstoće mazivog sloja, utjecaj na brtvene materijale i dr.). Zatim slijede primjenska ispitivanja gdje se u radnim uvjetima ocjenjuje trošenje maziva ili opreme. Treći stupanj je ocjena ekonomičnosti kroz potrošnjom goriva u vožnji. Ova ispitivanja provode se kroz zajedničkim programima proizvođača aditiva odnosno maziva i proizvođača vozila ili opreme. Rezultat tih ispitivanja je odabir i preporuka od proizvođača opreme (vozila) za prvo punjenje ili ugradnju. Za plasman zupčaničkih ulja važno je izdavanje odnosno posjedovanje dopuštenja za primjenu (approvala).

Primjer jednog ovakvog programa je ispitivanje koje je provedeno na 176 kamiona u 9 različitih krajeva SAD (teritorijalno) a u koji su bili uključeni veliki svjetski proizvođači aditiva i maziva s proizvođačem prijenosnika i prijevozničkom kompanijom. Ispitivana su po dva ulja s produljenim radnim vijekom prema zahtjevima specifikacije MIL-PRF-2105E: AO-1 i 2 (axle oil), API MT-1:TO-1 i 2 (transmision oil). Paralelno su ispitivane formulacije na osnovi mineralnog ulja II. grupe s boratnim aditivom te formulacije na osnovi polialfaolefina i estera s S/P aditivom. Rezultati su pokazali da su obje formulacije dale podjednaka svojstva a značajno je da su izdržale više od 1000000 km iako se od ovog tipa maziva očekuje duljina radnog vijeka 800000 km.

Ulja za industrijske zupčaničke prijenosnike

Razvoj maziva za industrijske prijenosnike je konstantan, prvenstveno ovisan o zahtjevima za visokim radnim svojstvima, tako da najnovije smjernice već prelaze svojstva svih poznatih standarda koja opisuju ulja za industrijske prijenosnike. U tablici 6 prikazane su klase kakvoće ulja za primjenu u industrijskim zupčaničkim prijenosnicima. Pažljivi odabir baznog ulja i aditivne tehnologije mogu zadovoljiti i najstrože zahtjeve za zupčanička ulja. Za najširu primjenu i dalje ostaju formulacije na osnovi mineralnog ulja uz dodatak aditiva. Aditivi su na osnovi sumpora i fosfora (S-P aditivi) sa svojstvom deemulgiranja i uz dodatak poboljšivača indeksa viskoznosti. Standardna klasa zadovoljava stroge specifikacija DIN 51517, David Brown S1.53.101. i USS 224 a time i ne sadrži aditiv na osnovi olova. Premium klasa, dodatno, zadovoljava i stroge testove oksidacije pri visokim opterećenjima.

Tablica 6: Razvoj ulja za industrijske zupčaničke prijenosnike

Table 6: Development of industrial gear oils

SLJEDEĆA GENERACIJA	zahtjevi još nisu utvrđeni	zahtjevi još nisu utvrđeni
TOP TIER/ VRHUNSKA- Povećana trajnost	FZG modificirana, mikropitting Nakon oksidacije – EP svojstva Nakon oksidacije - deemulzivnost Pjenjenje - uz zagađivala	Poboljšana zaštita od trošenja i otpornost na povišene temperature Produžen radni vijek Poboljšana svojstva protiv pjenjenja u zagađenom okolišu
PREMIUM- Termička stabilnost	Test čistih zupčanika (25 sati L-60) Oksidacijski test čistih površina	Minimalno curenje brtvi Minimalan talog Podmazivanje maglom
	US Steel 224 DIN 51517 DB S1.53.101	Deemulzivnost, AW/EP zaštita zupčanika,
STANDARD	AGMA 250.04 (9005-D95)	otpuštanje zraka
MINIMUM	US Steel 222 AGMA 250.03	Zaštita zupčanika
KLASA/STUPANJ	STANDARDI /METODE	RADNA SVOJSTVA

Vrhunska klasa mora zadovoljiti i primjenska svojstva dugog radnog vijeka pri visokotemperaturnim stresovima s dugotrajnim svojstvom deemulzivnosti, otpornosti pjenjenju uz prisutnost zagađenja te visokom sposobnošću zaštite od trošenja. Za osobito teške uvjete, iznimno, mogu se primijeniti tzv. kruta maziva ali ona koja će manje štetiti okolišu. Formulacije na osnovi sintetičkih ulja primjenjuju se tamo gdje mineralna formulacija ne može zadovoljiti, primjerice pri ekstremno visokim/niskim radnim temperaturama ili ekstremnim uvjetima trošenja ili gdje se traže posebna svojstva kao dulji radni vijek, biorazgradljivost, nezapaljivost i dr. Zastupljenost sintetičkih baznih ulja u industrijskim zupčaničkim uljima je: PAO 45 %, esteri 25 %, poliglikoli 10 %, alkilbenzeni 5 %, ostali (FE+PB) po 5 %.

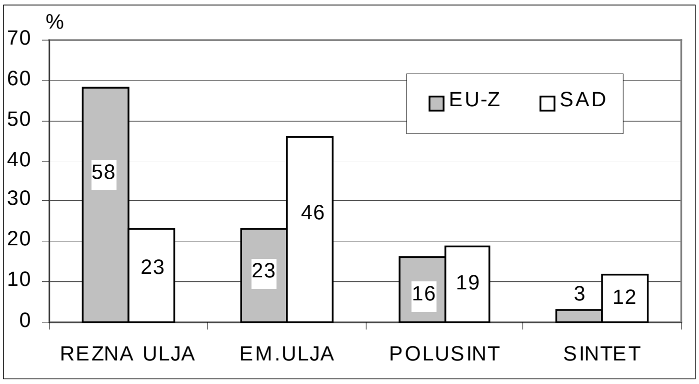
Tekućine za obradbu metala

Od ukupne svjetske potrošnje tekućina za obradbu metala (oko 2,2 mil.t) za operacije odvajanjem čestica upotrebljava se 53 %, za obradbu oblikovanjem 29 %, pri termičkoj obradbi 11 % i 7 % u zaštiti metala.

Zastupljenost tekućina za obradbu metala prema vrsti (rezna ulja, emulgirajuća ulja, polusintetičke i sintetičke tekućine za obradbu) i potrošnja u Americi i Europi (zapadnoj) prikazana je na slici 3.

Slika 3: Potrošnja tekućina za obradbu metala u SAD i Europi (zapadnoj)

Figure 3: Consumption of metalworking fluids in USA and Western Europe



Utjecajni faktori na razvitak tekućina za obradbu metala odvajanjem čestica su:

- razvitak novih strojeva za obradbu metala

- razvitak novih materijala - kompoziti, keramika
- povećanje radnih brzina i broja obrađenih dijelova
- kompatibilnost s drugim tipovima maziva, materijalima
- primjena tekućina koje se miješaju s vodom
- briga o utjecaju na okoliš
- briga o zdravlju ljudi
- troškovi za sigurno zbrinjavanje otpadnih tekućina
- smanjenje troškova održavanja

Tablica 7: Granične vrijednosti za komponente tekućina za obradbu metala (isječak)

Table 7: Limit values for metalworking components (excerpt)

ŠTETNI SPOJEVI	GRANIČNE VRIJEDNOSTI		ZAKON
	zrak, TRGS 900	TZOM	
Sekundarni amini	-	≤ 0,2 % (koncentrat)	TRGS 611
Barij (soli)	0,5 mg/m^3	≤ 10 ppm (koncentrat)	
Dietanolamin(2,2.iminodietanolamin)	15 mg/m^3	≤ 0,2 % (koncentrat)	TRGS 611
Nitrit i i spojevi	-	zabranjen ≤ 20 mg NO_3/l (em., otop.)	TRGS 611
Klorparafini (kloralkani)	-	≤ 0,2 %	Zakon o otpadu i TRGS 905
PCB, PCT	1-0,5 mg/m^3	≤ 4 ppm	Zakon o otpadu
1,2-Bbenzoizotiazol-3(2H)-on		≤ 0,05 % (emulzija, otopina)	25. ATP deklarirati R 43 iznad 0,05 %
Benzo-α-piren (PAH/PAK)	0,002 mg/m^3	50 ppm	21. ATP
1,3,5-tris-(2-Hidroksietil)-heksadidro-1,3,5-triazin (HHT)		≤ 0,1 % (emulzija, otopina)	25. ATP deklarirati R 43 iznad 0,1 %
Aerosoli i pare	5 mg/l (zrak) 20 mg/l (emulz.)		

*(21. ATP EU Directive 96/65/EG od 11.10.1996.

25. ATP EU Directive 98/98/EG od 18.9.1998.

67/548/EWG - Dangerous Substance Directive, Osnovna i specijalne, od 16.8.1967.

TRGS 611 - Technische regeln fuer Gefahrstoffe "Granične vijednosti za vodomješive tekućine za obradbu metala, ako se mogu razviti N-nitrozoamini" 2/2000.

TRGS 905 - Popis spojeva koji su kancerogeni, koji mijenjaju nasljedne osobine i koji utječu na plodnost, 2/2000.)

Spojevi na osnovi klora

Klorni spojevi se još uvijek mogu naći u primjeni ali u Europi znatno manje nego u Americi. Europska unija je svojom direktivom ECC 793/93 – zabranila primjenu klornih spojeva u tekućinama za obradbu metala i preradu kože. Umjesto njih traže se zamjenki spojevi. Klorparafini, široko primjenjivani i najpoznatiji EP aditivi u tekućinama za obradbu metala još uvijek se proizvode u SAD-u a proizvođači su jaki. Oni mogu biti štetni tijekom primjene i pri zbrinjavanju otpada. Naime, pri visokim tlakovima i temperaturama na dodirnim površinama te pri nižim režimima spaljivanja otpada mogu se razviti klorovodik i dioksini. Prema veličini molekule klorirani parafini se dijele na tri grupe: klorparafini s kratkim ugljikovodičnim lancem, sa srednjim i s dugim lancem. U tablici 8 je prikazana klasifikacija klorparafina i okvirni sadržaj klora u odgovarajućoj molekuli.

Tablici 8: Klasifikacija klorparafina i okvirni sadržaj klora

Table 8: Chlorinated paraffine grades and chlorine content

GRADACIJA KLORPARAFINA	DULJINA LANCA	SADRŽAJ KLORA, %
kratkolančani	C10 - C13	< 40; 40 – 49; 50 – 59; 60 – 69; >70
srednjolančani	C14 - C17	
dugolančani	C18 - C30	

Zbog sumnji u preranu zabranu primjene klorparafina i nemogućnosti pronalaska odgovarajuće zamjene ovog aditiva kod nekih primjena intenzivirana su ispitivanja štetnosti klorparafina. Dokazan je rizik od kratkolančanih Cl-parafina. Akutna toksičnost je vrlo mala a kod ponovljenih doza uočena su oštećenja jetre. Na genetička, teratogena, reproduktivna svojstva nema djelovanja. Pri ispitivanju kancerogenosti kratkolančani su pozitivni na jetri, štitnjači, bubrezima dok su dugolančani negativni. Na kožu nema djelovanja. Rezultat ispitivanja efekta na okoliš je smanjenje života vodenih organizama. Pokazali su i svojstvo bioakumulacije u školjkama.

Zbog velikog rizika od klorparafina proizvođači klorparafina, neki proizvođači i potrošači kemikalija razvili su program posebnih mjera zaštite i kontrole a isto tako i gospodarenja proizvodima na osnovi klora.

Utjecaj maziva na ljude tijekom primjene

Od profesionalnih bolesti pri radu s mazivima najčešće su bolesti dermatitis i respiratorne bolesti. Dermatitis ili oboljenje kože javlja se u tri oblika a to su: iritacija, kronična dermatoza i alergija. To je reakcija kože kao barijere organizma pri dodiru s mazivom. Respiratorne bolesti (astma, bronhitis) rezultat su djelovanja uljne magle ili aerosola koji se razvijaju u pogonima djelovanjem povišenih temperatura, visokih brzina i sl. Između maziva (magla, aerosol) i stanice respiratornog sustava dolazi do kemijske reakcije. Od profesionalnih dermatoza u metalo-prerađivačkoj industriji, u Njemačkoj 30-50% dermatoza rezultat je dodira s tekućinom za obradbu metala. Uzrok mogu biti komponente same tekućine ali, češće, zagađenja koja tijekom rada ulaze u radnu tekućinu. To su “strano” ulje, mikroorganizmi, sitne čestice metala i materijala iz alata, sredstva za konzerviranje obradaka, sredstva za čišćenje i dr.

Za ocjenu djelovanja komponenata na ljude koji imaju probleme vrše se ispitivanja sljedećim metodama: epikutan test, otvoren i zatvoren, Duhring Kammer test, Transepidermalni testovi, RBC test (red blood cell), BUS test (bovine udder system) i dr. Ispitivanja rade ovlaštene medicinske ustanove.

Mjere zaštite kože mogu biti medicinske ili tehničke. Značajan dio medicinske zaštite je rano otkrivanje uzroka koji je esencijalan za sprječavanje budućih dermatoza. Plan zaštite kože obuhvaća izbor sredstava za zaštitu kože, za čišćenje te njegu kože prema specifičnostima radnog mjesta. Od tehničkih mjera najvažnije je sprječavanje dodira a zatim primjena zaštitne opreme: odijela, rukavice, naočale i dr. Od osobite važnosti je izbor maziva manje štetnih za zdravlje a zatim i mjere održavanja.

Utjecaj vode na kakvoću maziva

Sadržaj vode u mazivima koja se za primjenu miješaju s vodom kreće se od 85 do 98 % te je razumljivo da je utjecaj vode iznimno velik. To su maziva koja se primjenjuju za obradbu metala, u hidrauličkim sustavima zatim zaštitna sredstva, sredstva za ispiranje i odmašćivanje i dr. Voda može uzrokovati stvaranje naslaga, povećanje korozije, destabilizaciju proizvoda, povećanje rasta mikroorganizama i sl.

Nepoželjan utjecaj vode sprječava se kemijski ili fizikalnim metodama. Utjecaj vode kemijski se može neutralizirati dodatkom tzv. “omekšivača” u proizvode ili izravno u vodu prije primjene. Zbog manjeg opterećenja okoliša prednost se daje fizikalnim metodama. Najpoznatije metode fizikalne pripreme vode su ionski izmjenjivači, ultrafiltracija, reverzna osmoza i destilacija. Ovisno o potrebnom kapacitetu priprava vode vrši se diskontinuirano u spremnicima ili kontinuirano ugradnjom u vodotok. Analizu vode treba obvezatno raditi prije rada a zatim i tijekom rada kada se koristi voda za nadoljev. Ispituju se sljedeća svojstva: pH, tvrdoća, vodljivost, sadržaj mikroorganizama, sadržaj klorida, sadržaj krutih čestica, itd. Učestalost analiza ovisi o vrsti pripreme i potrebnoj primjeni.

Životni vijek i analiza maziva

Budući razvitak osniva se na načelu regeneracijske sposobnosti prirode pri čemu se misli na štednju energije, očuvanje prirodnih izvora, reduciranje otpada, promjenu proizvodnog društva: izbjegavanje odbacivanja proizvoda zbog izobilja ili nove proizvodnje. Ostvarenje ovih ciljeva zahtijeva promjenu navika i davanje prednosti zatvorenim kružnim tokovima, dugovječnosti proizvoda, optimalnom iskorištavanju izvora te mogućnosti ponovne primjene (reusing) prije zbrinjavanja. To je utjecanje na vijek trajanja proizvoda. Zbog toga je važno određivanje životnog odnosno radnog vijeka maziva. Degradacija svojstava maziva odnosno stupanj trošenja tijekom primjene ili ocjena preostalog radnog vijeka ispituje se različitim metodama. Određivanje stupnja trošenja maziva može se provesti modeliranjem ili eksperimentalno. Ocjena istrošenosti najčešće nije jednoznačna i stoga se u praksi koriste različite metode u kombinaciji. U tu svrhu razvijaju se i nove metode koje će biti jednostavnije i brže jer je bitno dobiti podatke što prije na mjestu primjene i to često na terenu. Zajednički nedostatak ovih metoda je što nisu standardizirane.

Mehanizam trošenja tribološkog sustava podmazivanja sastoji se od trošenja dodirnih površina i trošenja maziva. Ako dolazi do trošenja dodirnih površina, prisutne su čestice trošenja. Trošenje masti (reološko trošenje masti) ili drugih maziva je nepovratna promjena svojstava maziva.

Za ocjenu preostalog radnog vijeka maziva koriste se klasične metode kao što su HPLC, FTIR, UV –spektroskopija, IPC i sl. Ovim metodama određuje se stupanj oksidacije, sadržaj ulja, sadržaj aditiva, kiselinski broj, bazni broj, promjena viskoznosti i sl.

Jedan od novih postupaka je metoda Linear Sweep Voltametry, LSV, koju su razvili SKF ECR i Fluitc. To je elektroanalitička metoda kojom se mjeri napon. Preostali aditiv reagira kemijski sa smjesom reagensa u otapalu, uglavnom antioksidansi: ZDTP, PANA, BHT. Prednost je u tome što je postupak jednostavan: uzorkovanje, miješanje s 5 ml reagensa, stavljanje u aparat i mjerenje. Potrebna je mala količina uzorka (najviše 200 mg) i nije potrebno ekstrahiranje uljne faze s otapalom. Kako je uređaj prenosiv, moguća je in situ analiza. Budući da je brza, metodaje pogodna za ispitivanje u primjenskim uvjetima, osobito, maziva za vozila, željeznice i sl.

BEQUIET TEST (SKF) ili određivanje bučnosti je metoda za mjerenje vibracija koje se javljaju zbog prisutnosti čestica. Pogodna je za ocjenu kvalitete maziva a zatim i čistoće te slabljenje svojstava. Poznato je da je debljina mazivog sloja ispod 1 μm svaka čestica većeg promjera ometa miran rad tribosustava i uzrokuje razvoj buke. Prema ovoj metodi masti su svrstane u četiri gradacije:

1. *dirty-zagađen* - tvrdoća i veličina čestica nakon dodira ostavlja trajna oštećenja - povećanje buke i smanjenje radnog vijeka ležaja,

2. *noisy-bučan* - tvrdoća i veličina čestica koja može oštetiti površinu ležaja i koja povećava buku,

3. *clean-čist* - tvrdoća i veličina čestica će dati određene vibracije ali nema trajnog oštećenja površine,

4. *quiet-tih* - najveća razina čistoće, najmanje čestice, minimalna vibracija.

U prvu grupu jako rijetko ulazi svježe mazivo, već su to obično maziva pri radu. Drugu grupu daje samo nekoliko masti na tržištu: na osnovi ugušćivača ili krutoga maziva (tipični primjer neke Ca kompleksne masti). U treću grupu obično ulaze masti na osnovi poliuree koje prave aglomerate ali oni ne uzrokuju oštećenja. U četvrtu gradaciju ulazi samo nekoliko masti i to na osnovi Li sapuna jer oni daju finu strukturu ili one masti koje su proizvedene u čistoj atmosferi. Ova metoda može se koristiti i pri razvoju masti kroz ocjenu čistoće. Cilj je proizvesti što tišu mast sa što manjim padom svojstava.

Ferografija je metoda kojom se izdvajaju čestice trošenja materijala iz uzorka ulja za podmazivanje. Čestice materijala, otkinute s radnih površina dijelova tribosustava, rezultat su djelovanja procesa trošenja.

Čestice trošenja izdvajaju se iz maziva na osnovi magnetskog privlačenja odgovarajućim permanentnim magnetima. Ferografska metoda se potvrdila kao uspješna tehnika za nadgledanje stanja zatvorenih triboloških sustava (motora, reduktora i sl.).

Uloga subjekata u primjeni maziva

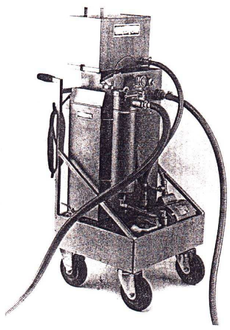
Proizvođači a također i korisnici maziva jednako su odgovorni za primjenu i produljenje radnog vijeka. Proizvođači su dužni poboljšavati formulacije proizvoda koje moraju biti manje štetne za zdravlje ljudi i okoliš, sa što duljim radnim vijekom, uz što jednostavniju njegu i održavanje te što jednostavnije zbrinjavanje otpadne tekućine. Proizvođač daje preporuke za njegu i održavanje, vodi brigu o kompatibilnosti s ostalim materijalima te daje preporuke za izbor maziva. Korisnici su dužni poduzeti mjere njege tekućine, radnog prostora i ljudi, sprječavanje zagađenja tijekom primjene, uklanjanje zagađivala iz radne tekućine te zbrinjavanje nakon rada. Potrošač mora osigurati što bolje održavanje konstrukcijskim zahvatima kao što su ugradnja pomoćnih strojnih elemenata: centrifuge, separatori, filtri, uređaji za omekšavanje vode, itd.

Proizvođači i potrošači maziva zajedničkim radom primjene i ispitivanja svojstava tijekom primjene rade na razvitku modernih formulacija. Ispitivanja mogu trajati i više godina. Osim dobitka najbolje formulacije za određene uvjete primjene, cilj zajedničkog ispitivanja su preporuke za globalnu primjenu određenog maziva od proizvođača strojeva ili dijelova opreme.

Tijekom rada i tekućine za obradbu metala i druga maziva valja kontrolirati s ciljem poduzimanja mjera korekcije za dobivanje zadovoljavajućih radnih svojstava. Za ispitivanje radne tekućine tijekom primjene valja napraviti plan i u ovisnosti o količini i vremenu analize raditi dnevno, tjedno, mjesečno. Također treba odrediti postupke njege i održavanja: osobna, stroja i tekućine, okoline, zaštitna sredstva. U slučaju potrebe korekcije radne tekućine daje se prednost fizikalnim metodama pred kemijskim. Na slici 4 prikazan je pokretni stroj za čišćenje radnih tekućina za obradbu metala čime se znatno produžava radni vijek tekućina. Održavanje valja planirati prije same odluke o primjeni cjelokupnog plana - menadžment plan.

Slika 4: Pokretni uređaj za čišćenje vodomješivih tekućina-maziva

Figure 4: Mobile machine for cleaning watermiscible fluids-lubricants



Funkcija održavanja u suvremenoj tvrtki

Funkcija održavanja je utjecanje na životni vijek prirodnih izvora, maziva i opreme. Temeljni cilj održavanja kao funkcije tvrtke je poboljšanje učinkovitosti tvrtke i sprječavanje štete za tvrtku. Suvremeno održavanje mora biti sustavno i procesualno mišljenje i djelovanje. Udio neplaniranih mjera održavanja mora se dovesti na nulu.

Od poznatih temeljnih strategija održavanja, uz korektivno i preventivno, daje se prednost prediktivnom održavanju kada se vrši intervencija prema stanju (Condition based maintenance). Analiza stanja opreme može se dobiti na mjestu primjene ugradnjom senzora i on-line kontrole. Analizu maziva mogu raditi proizvođači maziva u okviru svoga tehničkog servisa ili se uzorci mogu transportirati u specijalizirane laboratorije. Na osnovi analizom dobivenih svojstava maziva se uspoređuju s dopuštenim granicama i nakon toga se vrši intervencija u tribološkom sustavu ako je potrebno. To može biti izmjena ili popravak maziva, oštrenje alata, popravak opreme navarivanjem i sl. Ovom vrstom održavanja smanjuje se ukupni trošak održavanja, utrošak rezervnih dijelova, ušteda radnih sati osoblja a istovremeno se poboljšava kakvoća proizvoda. Razvitkom senzorske tehnike dolazi se do proaktivnog održavanja.

Kompjutorska tehnologija i elektronski putevi informacija kao i razvitak postupaka modeliranja omogućavaju i nove tehnike primjene maziva. Tako se na osnovi baze podataka razvila tehnika praćenja potrebe za mazivima i preporuka kao cjelokupno gospodarenje mazivom TFM (total fluid management) u Njemačkoj KUSI projekt i dr. Primjena ove tehnike dovodi do smanjenja angažmana djelatnika u proizvođačkoj tvrtki ali i do smanjenja potrebe za djelatnicima što za neke tvrtke može biti katastrofalno.

Kruta maziva, prevlake i kompoziti

Potreba za mazivom za primjenu pri ekstremno visokim temperaturama, radijaciji, vakuumu i ostalim ekstremnim okruženjima i uvjetima doveli su do razvitka nanošenja krutog mazivog filma na dodirne površine. Kruta maziva su se pojavila krajem 1940. godine a sada se primjenjuju u različitim dijelovima industrije, autoindustrije te vojnoj i avio industriji. Uobičajena kruta maziva su molibden disulfid (MoS_2), grafit, politetrafluoretilen (PTFE), volfram disulfid (WS_2), olovo i dr. Molibden disulfid i grafit imaju niski koeficijent trenja i visoki kapacitet nošenja opterećenja. PTFE pokazuje najniži koeficijent trenja ali niski kapacitet nošenja opterećenja. Grafit nije dopušten za primjenu prema većini vojnih specifikacija jer uzrokuje galvansku koroziju. Također je poznato da molibden disulfid može uzrokovati koroziju u slučaju primjene gdje radne temperature prelaze 350^{0}C. Pri toj temperaturi MoS_2 oksidira i stvara sulfatnu kiselinu. Korozija se može pojaviti i u drugim radnim uvjetima te ih je jako bitno poznavati u slučaju primjene krutih maziva. Primjenjiva su u uvjetima gdje je problematično nanošenje i ostanak konvencionalnog maziva, gdje je prisutna prašina i zagađivala, gdje su radne temperature od –67 do +93 ^{0}C i sl. Olovo i antimon se zamjenjuju jer se kao teški metali smatraju štetnima za zdravlje i opasnim otpadom.

Prevlake su materijali sa svojstvom podmazivanja, koji su naneseni na površinu nekom od odgovarajućih metoda. Debljina je u području do nekoliko mikrometara. Smatraju se trećim tijelom tribosustava.

Moderna mehanička industrija suočena je s izazovom povećanja zahtjeva radnih svojstava preciznih kliznih komponenata uz minimalne konstrukcijske promjene. To je moguće postići primjenom tankog filma prevlaka koji doprinose smanjenju trenja i trošenja. To su DLC (diamond-like carbon), PVD (physical vapour deposition): TiAlN, CrAlN, ZrN, ZrC i dr. Mogu se nanijeti na konstrukcijske materijale kao što su čelik, aluminijeve slitine, titanove slitine i dr. Primjena pokriva polja hidrauličkih preciznih komponenata, motora, transmisija i ostalo.

Kompozitni materijali, MMC (metal matrix composite) koriste se kao zamjena za metal. Imaju odlična svojstva kao što je otpornost prema trošenju i koroziji, otpornost na vlagu, lakši su od metala te su lakši za transport i manipuliranje. Imaju i ekološke prednosti u uštedi na težini te brzini rada. Nalaze primjenu u autoindustriji, papirnoj industriji, agrikulturi pri obradbi metala i dr. Sadržaj čestica krutog maziva mijenjaju karakteristike kompozita. Od novih materijala značajna je primjena i tzv. metalnih pjena koje se proizvode od otpadnih materijala, imaju odlična mehanička svojstva i malu težinu.

Sloj krutog maziva, prevlake, kompoziti, keramika i moderni materijali primijenjeni u tribološkim sustavima, na materijalima za obradbu ili na alatima omogućavaju podmazivanje sa smanjenom količinom konvencionalnog maziva (MQL) a u nekim slučajevima i suho podmazivanje (bez maziva). Podmazivanje bez maziva ima ekološke prednosti ali ima i nedostatke. Suho podmazivanje, primjerice, ne može riješiti odnošenje čestica ili odvođenje temperature i u tim slučajevima primjene tekuće podmazivanje je i dalje nezamjenjivo.

Zaključak

Zdravlje, sigurnost pri radu i zaštita okoliša glavni su pokretači razvitka maziva na početku novog tisućljeća. S tim ciljem valja zamijeniti niz spojeva koji se nalaze u širokoj primjeni a za koje je poznato da su štetni zdravlju ili za okoliš. Isto tako valja primjenjivati i bazna ulja manje štetna za okoliš i ljude. Primjena prirodnih ulja u funkciji aditiva i baznih ulja u budućnosti će imati veliku prednost. Ukoliko se ne mogu zamijeniti, sigurnosni zahtjevi nalažu označivanje sadržaja štetnih spojeva te mjere za postupanje tijekom pripreme, primjene i nakon primjene kada postaju otpad.

U budućnosti će kao doprinos održivom razvitku potrošnja maziva biti sve manja a time i manja količina otpada. Zbrinjavanje otpada treba biti što jednostavnije dok je biorazgradljivost jedan od osnovnih zahtjeva za maziva budućnosti. Općenito, moderna maziva moraju zadovoljiti sve više zahtjeva i sigurnosnih i tehničkih. Razvitkom moderne tehnologije i materijala količina potrebnog maziva sve je manja a često se daje prednost minimalnom ili suhom podmazivanju.

Maziva su kvalitetnija, ali su i cijene maziva sve više. Na primjenu maziva ne može utjecati samo cijena maziva. Izbor i primjena maziva mora obuhvatiti kompletno gospodarenje mazivom od formulacije, proizvodnje, primjene, ispitivanja, mogućnosti ponovne primjene pa do zbrinjavanja. Osim proizvođača i potrošača maziva, distributera proizvodima ili otpadom, za budući razvitak odgovorna je i gospodarstvena politika i zakonodavstvo pojedine zemlje ili unije.

LUBRICANTS, MATERIALS AND LUBRICATION ENGINEERING

ABSTRACT

The past century and the end of the millennium have been marked by a rich development of technique, technology, materials and lubricants. However, the last years of the former century have shown that not only the technological advancement and economic development have social significance, but also environmental protection and human health. Energy saving and natural resources have become the central environmental protection concern. Public concern about lubricants has been *raised because each year 40-50% of around 5 million tons of used lubricants ends up in the environment instead of being recycled using any of the available methods.*

The goal is to develop tribological systems that are less environmentally harmful, while at the same time offering high performances. This is possible to achieve by applying new materials or coats over the contact surfaces or by applying less environmentally and health hazardous lubricants with high performances. Apart from that, development of informatics and numerical methods, as tools for designing the tribological system, as well as a rich database and new maintenance and testing methods, guarantee improved application.

Introduction

The central component of the tribological system is the lubricant, whose most significant function is the lowering of friction and wear appearing in the contact of two surfaces in relative motion. As a subsystem, tribological systems are integrated everywhere into the technical systems. Apart from more significant applications in internal combustion engines, transmission, and hydraulic systems, there is also a large number of further applications. Due to the poor execution of the tribological system or inadequate application, if it is not fit for the given system, commercial losses may occur measured in billions of euros annually. That is why the significance of the tribosystems is not only technical, but also economic and environmental. The concept of the future successful development endeavours to associate economy and ecology into a complex and non-contradictory system. Technological advancement and innovative research makes this possible, acting as the basis for intensifying the environmental aspects in the future technical subjects. The paths of lubrication development in the past century, based on the development of scientific disciplines and dependent on the needs of industry and equipment, are shown in Figure 1.

By recognizing the function of the tribological system and through a rich development of materials, equipment and methods, it seemed that all the problems associated with lubrication have been resolved. However, lubrication engineering still remains active. The goal is to develop tribological systems that will be less environmentally harmful, while at the same time having high technical performances.

Development of technical products is dependent on a number of both general and specific requests. General requests are: (environmental) compatibility, high technical performances, application efficiency of lubricants, structure and materials, and lubricant price i.e. economical character.

Specific requirements are: reduced need for fluids/lubricants - compensation by materials, application of natural or chemically modified natural stocks, production of lubricants at reduced cost, use of databases or numerical methods, saving of energy and natural resources. The lubricant's economical character does not entail only its purchase price, but is also the result of evaluating a series of properties. These are compatibility (multifunctional lubricants), ageing and temperature stability, oil change interval, possibility of recycling, management costs, maintenance measures, investments into machinery, and also estimation of operating and storage expenses, emission control measures, health protection and occupational safety measures, simpler procedure for obtaining approvals for application, and reduction of costs for managing oil spills and their cleanup.

Lubricant formulation in the new milennium

Liquid or conventional lubricants generally consist of base oil – most frequently in the amount of around 90 %, and additives - around 10 %. Base oil may be of mineral origin, synthetic, or natural (vegetable and animal).

Over the past around 20 years, the quality of mineral base oils has changed significantly. The first reason is the fact that crude oil sources have changed, while the other is concern for environmental protection and human health. Formerly they used to contain more aromatics and were considered cancerogenous. The quality has improved through solvent refinement and hydrotreatment, as well as with the development of new synthetic procedures. The third reason for oil quality advancement lies in increased requirements for the functional properties of lubricants, for instance motor oils, such as better oxidation stability, flow properties, viscosity, and the like.

Table 1: API Classification of base oils and basic properties

API GROUP	Saturated hydrocarbons,%	Sulphur,%	Viscosity index
GROUP I, solvent-refinement	below 90	> 0,03	80 – 120
GROUP II, hydrotreatment	> / = 90	< / = 0,03	80 – 120
GROUP III, deep hydrotreatment / wax isomerization	> / = 90	< / = 0,03	120 +
GROUP IV, polyalphaolefins (PAO) polymerization, hydrogenation	defined formula $R\text{-}CHCH_3\text{-}/CH_2\text{-}CHR/_X\text{-}H$	-	130 +
GROUP V	⇒ All other base oils (including those synthetic)		

Table 1 shows the types and basic properties of base oils according to API (American Petroleum Institute) classification.

High performance requirements for lubricants have led to an increased application of synthetic base oils such as polyalphaolefins, esters, and so on. In Table 2 the properties of synthetic oils are presented in comparison with mineral oil.

Table 2: Performance of synthetic lubicants compared to mineral oils

PROPERTIES/ REQUIREMENTS	Mineral oil	Synthetic oils						
		Synthet. hydrocarbons			Organic esters			
	paraffi n	PAO	PIB	DAB	DAE	POE	PG	PhE
Viscosity interval	wide	very wide	very wide	low	low	low	very wide	low
Viscosity/ temperature relation	2	4	3	2	3	3	5	1
Low temperatures	1	4	2	3	3	3	4	2
High temp. stability with inhibitor	2	4	3	3	3	5	3	2
Compatibility with mineral oil	5	5	5	5	3	2	1	1
Low volatility	2	5	3	3	5	5	3	3
Compatibility with paint/varnish	5	5	5	5	2	2	3	1
Hydrolitic stability	5	5	5	5	2	2	4	2
Shear stability	5	5	3	5	5	5	5	5
Lubricating properties	2	4	2	2	3	3	4/5	5
Anticorrosion properties with inhibitors	5	5	5	5	3	3	3	2
Additive stability	5	3	3	5	4	4	2	3
NBR compatibility	5	5	3	5	2	2	3	2

*(PAO = polyalphaolefin, PIB = polyisobutylene, DAB = dialkylbenzene, DAE = diacid ester, POE = poliolester, PG = polyglycol, PhE = phosphateester, NBR= acrylonytril-butadien rubber)

**(5=excellent, 4=very good, 3=good, 2=satisfactory, 1=poor)

Under extreme operating conditions, for instance those climatic-low temperatures, it is possible to apply polyalphaolefins. PAOs are used at the most, in all areas: in industry, aviation industry, in greases, hydraulic fluids, gear oils, and so on. In the application of PIBs and alkylaromatics, one may observe some limitations, but they still play an important role as additives to the base oil. Synthetic lubricants are always recommended in situations where they ensure a positive balance of costs regardless of the high stock price. Figure 2 shows the cost factor on the example of a hydraulic fluid depending on the base oil type: HEPG – polyglycols, HEES – z saturated esters, HEES - n unsaturated esters, HETG – vegetable oil (triglicerides), MO- mineral oil.

Impact of legal acts and various associations' recommendations on lubricants

While formulating modern lubricants, one must take into account the impact of individual components on human and environment. Environmental and health impact of lubricants is defined by the following properties: toxicity, biodegradability, inhibition (microbial) and bioaccumulation. The impacts are regulated by various legal standards or recommendations with mandatory implementation in given states or groups of states, various associations, and consumers. Since, in spite of various laws and recommendations, it is impossible for them to keep pace with the increasingly rapid scientific development, lubricant manufacturers need to continuously follow new achievements and tendencies in the estimation of individual substances' toxic activity.

Table 3: Safety requirements for lubricants examination

				…	(386TE)
				teratogeneity	
				…	
				mutageneity	
				toxicity/kinetic	
				…	
		…	(42TE)	toxicity/algae	
		Bioaccumulation		Bioaccumulation	
		Sensitivity		Sensitivity	
		toxicity/dermal		toxicity/dermal	
….	(8TE)	Daphnie/bacteria		Daphnie/bacteria	
irritation		irritation		irritation	
toxicity/oral		toxicity/oral		toxicity/oral	
toxicity/fish		toxicity/fish		toxicity/fish	
biodegradability		biodegradgability		biodegradability	
testing	cost	testing	cost	testing	cost
YESTERDAY		TODAY		TOMORROW	

This is of particular importance in the area of metalworking fluids, for human at workplace comes into direct contact, primarily with hands, while servicing the machine, then by splash, and finally by breathing in. The concern about the toxicity of individual components used in lubricant formulation has been defined through maximum permissible concentrations (MPC) in product, working environment (atmosphere) or waste (when discharged into watercourses or air). This has lead to the development of new technological branches: occupational medicine, ecotechnology and processing technology. The kinds of testing lubricants' environmental impact are expanding and becoming increasingly sophisticated, but also costlier. Table 3 provides a review of some mandatory tests, the order of introduction, and the testing cost estimate (in thousands of euros TE). The Technological Safety Sheet, obligatory for every lubricant, contains properties associated with environmental and human health, possible threat, prevention of contact, first aid, transport properties, etc.

Significant is the impact of the German Environmental Responsibility Act from 1991, which has - among other things - introduced the principle of the causer, the obligation to inform, and the obligation to undertake precaution measures and measures of restoration to the original condition. The Waste Act from 1996, having integrated a part of the Recycling Act, has introduced the oligation for lubricant manufacturers to organize collection of waste motor and gear oils from the consumer. Lubricant manufacturers most frequently use authorized servicing garages for oil collection. Collection, management or recycling costs are most frequently covered by lubricant consumers (between 100 and 200 E/t). Furtherly, the law makers have defined several categores of waste according to chlorine (0.2 %) and PCB content that need to be managed as prescribed, rendering the waste management costs considerably higher. High waste management costs lead to the development and application of biodegradable lubricants, and lubricants free of chlorine and other noxious compounds.

Environmentally less harmful lubricants

What is happening with lubricants after the expiry of their service life? It is estimated that around 5 million tons of used lubricants is generated every year. The most part is collected as waste oil: 47 %; lubricant loss in circulaton systems is 28 %, regeneration or disposal on the waste oil generation spot is 11 %, complete or partial incineration in internal combustion engines is 6 % and 8 % is the total loss lubrication. It may be observed that 58 % is being managed, while 42 % is being lost in the environment, which means that around 2 mil t of lubricants are polluting it.

This is the reason for an increased development of environmentally adapted lubricants, EAL. Such lubricants shall reduce the costs of management, water protection, maintenance, interphase cleaning, water reconditioning after splitting, and so on. EALs are also usually non-toxic, while they also posses better skin compatibility. The properties of environmentally adapted lubricants are:

- fast biodegradability
- low water pollution degree
- poor water solubility
- unharmfulness or low toxicity
- heavy metals-free additives
- non-incineration/high flash point, water fluids
- low volatility – high flash point
- application of natural feeds – ester oils, rapeseed, soya oil, animal oils

Environmentally adapted lubricants are applied on spots where they are entirely lost into the environment, the so called total-loss lubrication. These are mobile hydraulic systems, lubricants for railroad switches, saws, concrete mould oils, and so on. They are also applied in industry: hydraulic, industrial gear oils, and the like. In formulations of EAL lubricants, the following additives should be avoided: compounds based on lead, chlorine, barium and zinc (such as ZDDP). Instead of them, applied are the phosphatic acid esters, alkylene carbamates, compounds based on “green” bismuth, and other non-harmful compounds. As base oils, one may use synthetic esters, polyglycols, and some other synthetic base components. Most desirable is the application of natural oils which may provide good properties for a lubricant as both additives and base oils.

During application, we have observed important changes in the activity of synthetic and natural components with regard to formulations with mineral oil. That is why tests have been increased, evaluating primarily the oxidation and temperature stability and the compatibility of the additive and the base oil component. Furtherly evaluated is their polarity, surface activity, chemical reactivity, the ability to create a lubricating film, wear protection, load carrying capacity, heat transfer, dependence of viscosity on temperature, and so on.

Hydraulic Oils

The consumption of hydraulic fluids in Germany in 1995 amounted to approximately 160000 t. Based on consumption classification per type, it is estimated that by 2005 there shall occur an increase in the consumption of minerally based oil in stationary systems, while that in mobile systems shall decrease (Table 4). Parallely, the mobile systems shall increase the consumption of fast biodegradable fluids, while the other shall remain on the same consumption level.

Table 4: Hydraulic fluid consumption and development (Germany, 1995)

1995	Hydraulic fluid type	2005
84 %	mineral oil based (HLP, HLPD, HD)	? stationary ↗
4 %	fast biodegradable (HETG, HEES, HEPG)	? mobile ↗ stationary ↘
7 %	fire resistant (HFC, HFA, HFDU)	7 % equal
5 %	others (PAO, HC)	5 % equal

Activities surrounding the specification of fast biodegradable lubricants have been speeded up. They must meet stringent technical and environmental requirements: from the equipment manufacturers' specifications, such as Caterpillar, Rexroth, Sauer Sundstrand, to the laws and recommendations by various associations in individual states.

Of significance are:

- The German “Blue Angel”, RAL UZ 79 (fast biodegradable hydraulic oils)
- VDMA Lists 24568, 24589 (VDMA, Association of German Equipment and Plant Manufacturers)
- Report by the German Ministry of Nutrition, Agriculture & Forestry
- ISO pre-specifications ISO L 6743-4 (ISO CD 15380)
- The Swedish DIN “Gothenburg Paper”
- The English “Environmental Agency”
- The “Canadian Environmental Choice Program”
- The Dutch “More Environmentally Friendly Lubricants” and others.
- The Europian Union still has no lubricants enlisted in its directive EU 880/92.

Hydraulic fluids of the future or fast biodegradable hydraulic fluids must meet not only the evironmental criteria, but also those technical, while the abstract is shown in Table 5.

Table 5: Future hydraulic fluids

VDMA Sheet 24568	“Blue Angel” environmental label, RAL UZ 79
Type: HETG, HEES, HEPG	fast biodegradable hydraulic fluid - RBHF
stress on technical properties	stress on environmental criteria
- low temperature properties	- no compounds requiring special labelling
- stability towards ageing	- eco-toxicological criteria
- compatibility with seal materials	- water pollution degree, WPC
- hydrolitic stability	- biodegradable
- Linde test, dry TOST	- technical properties matching VDMA 24568

Lubricating Greases

Mineral oil is still the dominant base oil for lubricating greases. They are increasingly being developed based on synthetic oils owing to better properties with regard to mineral oils, such as oxidation stability, flow at low temperatures, high temperature properties, compatibility with plastic, conductivity, and so on. Synthetic greases also have a few weaknesses. For instance, silicon oil has a better temperature viscosity range, but is poor at boundary steel lubrication. Polyphenilether has a high price and poor low temperature properties. Better for application are diesters, poliolesters, polyalphaolefins, alkyldiphenil esters, and so on. The choice of base oil for the production of greases is dependent on application properties, while, for those biodegradable, esters are applied. In the greases of the future, the following additives are to be avoided: Pb, Cl, Ba, Zn (as ZDDP) compounds. In the thickener system, one may apply “functional polymers” (0.5%), acting as improvers of adhesion/cohesion, water resistance, soap structure, or other properties.

Gear Oils

Vehicle manufacturers are the main promoters of vehicle gear oil lubricants. The main purposes are evaluated through economic fuel consumption, prolonged oil fill intervals, prolonged equipment service life, and reduced maintenance costs.

The trend for the new millenium – the vehicle manufacturers' competition game: advanced aerodynamism, higher speeds, lower RPM, higher torque power and larger lots. The automotive oil service life is at least 100000 km, and, for heavy-duty vehicles, 800000 km. The oil is required to perform within a broad temperature interval, in turn requiring advanced rheological properties of the lubricant. These are the tasks to be resolved by OEMs and by lubricant i.e. additive manufacturers. Requirements are made regarding lubricant composition: additives based on sulphur and phosphorous (S-P additives) or boron (B), with the addition of viscosity index improvers (VI) and antioxidants. Gear oils may be single grade and multigrade; minerally based, semi-synthetic or synthetic.

Testing is an important factor for gear oils and is performed in three stages. The first are the laboratory tests using standard methods (ASTM, DIN), and tests on bench test rigs, those using special methods (dynamic-mechanical tests for determining the lubricating film load carrying capacity, impact on seal materials, and the like). They are followed by applicative tests where lubricant or equipment wear is evaluated under operating conditions. The third phase is the cost-effectiveness evaluation through fuel consumption – in field tests. These tests are conducted through joint programmes by additive i.e. lubricant manufacturers and vehicle or gear manufacturers. The result of these tests is the choice and recommendation by the equipment (vehicle) manufacturer for the first fill or factory fill. The marketing of gear oils requires the issuing i.e. possession of the application approval.

An example of such a programme is the test performed on 176 trucks in 9 different parts of the USA (territorial), including large global additive and lubricant manufacturers, a gear manufacturer, and a transportation company. Tested were two oils each time with a prolonged service life according to the requirements of the specification MIL-PRF-2105E: AO-1 i 2 (axle oil), API MT-1:TO-1 and 2 (transmision oil). Tested parallely were the formulations based on mineral oil 2^{nd} group with a boron additive, and formulations based on polyalphaolefins and esters with a S/P additive. The results have shown that both formulations have given approximately the same properties, while it is significant that they have lasted over 1000000 km, although this particular lubricant type is expected to have the service life of 800 000 km.

Oils for Industrial Gear Transmissions

Development of lubricants for industrial gear transmissions has been a constant one, dependent primarily on high performance requirements, so that the latest guidelines already exceed the properties of all the known standards describing oils for industral gears. Table 6 presents oil quality classes for application in industrial transmissions. A careful selection of the base oil and additive technology may meet even the most stringent requirements imposed upon gear oils. As regards the widest application, there are still formulations based on mineral oil, plus additives. Additives are based on sulphur and phosphorus (S-P additives), with demulsifying properties and with the addition of viscosity index improver. The standard class meets the stringent specifications DIN 51517, David Brown S1.53.101. and USS 224, not containing any lead based additives. The premium class additionally meets also the stringent oxidation tests at heavy loads. The top class must meet also the application properties of a long service life under high temperature stresses with a long-term demulsifying properties, resistance to foaming, with the presence of pollution and a high antiwear capacity. As for extremely heavy conditions, one may exceptionally use the so called solid lubricants, but definitely those environmentally adapted.

Table 6: Development of industrial gear oils

THE NEXT GENERATION	?	?
TOP TIER/ TOP Increased durability	FZG modified, micropitting After oxidation – EP properties After oxidation - deemulsifying Foaming – with pollutants	Improved wear protection and resistance to increased temperatures Prolonged service life Improved antifoaming properties in polluted surroundings
PREMIUM- Thermal stability	Clean gear test (25 hrs L-60) Clean surface oxidation test	Minimal seal leakage Minimal sludge Lubrication by mist
	US Steel 224 DIN 51517 DB S1.53.101	Deemulsifying, AW/EP gear protection,
STANDARD	AGMA 250.04 (9005-D95)	air release
MINIMUM	US Steel 222 AGMA 250.03	Gear protection
CLASS/DEGREE	STANDARDS/METHODS	PERFORMANCES

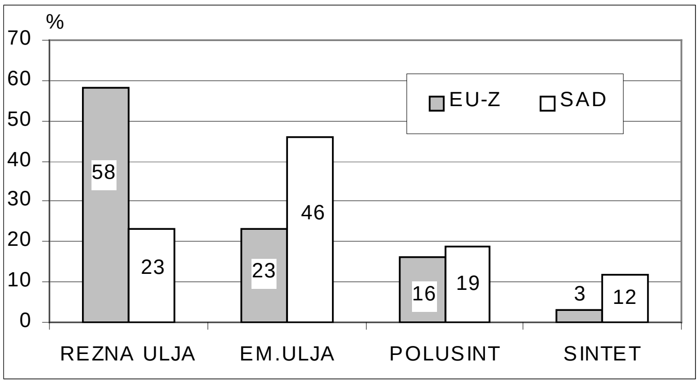
Formulations based on synthetic oils are applied where the mineral formulation cannot satisfy - e.g. at extremely high/low operating temperatures or extreme conditions of wear or where special properties are required, such as prolonged service life, biodegradability, nonflammability, and so on. The share of synthetic base oils in industrial gear oils is as follows: PAO 45 %, esters 25 %, polyglycols 10 %, alkylbenzenes 5 %, others (FE+PB) po 5 %.

Metalworking Fluids

Out of the total global consumption of metalworking fluids (around 2.2 mil.t), 53 % is used for operations using particle separation, 29 % for treatment by forming, 11 % at thermal treatment and 7 % in metal protection.

The share of metalworking fluids per type (cutting oils, emulsifying oils, semi-synthetic and synthetic metalworking fluids) and consumption in America and Western Europe is shown in Figure 3.

Figure 3: Consumption of metalworking fluids in USA and Western Europe



The factors impacting the development of metalworking fluids using particle separation are:

- development of new metalworking machinery
- development of new materials - composites, ceramics
- increase of operating speeds and number of worked pieces
- compatibility with other lubricant types and materials
- application of water miscible fluids

- environmental impact concern
- human health concern
- costs of the safe management of waste fluids
- maintenance costs reduction

New formulations of metalworking fluids, neat oils and water miscible fluids, do not contain chlorinated paraffins which are replaced by phosphates, sulphonates, esters, and the like. The content of aromatic hydrocarbons in base oil, (application of base oils without aromatics) and sulphur content have been reduced. Advantage is given to natural oils (vegetable and animal triglicerides) as additives and base oils. The application of synthetic oils is recommended for specific spots, if one wants biodegradability or non-inflammation. In case of high speeds, as in high speed operations when oil mist is created, it is possible to apply additives for preventing oil mist, but the advantage is given to the choice of a high quality base oil, with lower volatility. Due to increased treatment speeds, advantage is given to lower viscosities of neat treatment oils or water miscible formulations. The lubricants need to be multifunctional where simultaneous lubrication is required when treating metals, slideways, hydraulics or power complex.

In case of miscible fluids with pronounced corrosion appearance of importance is the replacement of excellent corrosion inhibitors: nitrite and diethanolamine (DEA), which are considered to react under application conditions by creating a cancerogenous compound N-nitrosodietanolamine. They are replaced by less harmful amines, such as: monoethanolamine (MEA), triethanolamine (TEA), diglycolamine (DG), aminomethylpropane (AMP), monoisopropanamine (MIPA), and the like. Surface active components, emulsifyer and corrosion inhibitors do not contain the aromatic ring, while boron content has also been reduced (< 2% in concentrate). Although boron is no longer on the list of undesirable compounds by the famous automobile manufacturer Mercedes Benz, attempts are being made to find a replacement feed for boron compounds. Laboratory research has started with the lactic acid, but the formulations have not been tested yet in application. One of the most significant European directives is associated with the addition of biocides, imposing the declaration of such compounds (98/8 EC) and resulting in reduced content of some biocides in formulations, and also for maintenance in tanks. Metal, especially cobalt secretion (Co) is an additional factor impacting the service life reduction of both the tools and the fluid, causing inhalation problems of the employees, as well as the problem of wastewater cleaning. Table 7 presents limit values for some components applied in metalworking fluids (MWFs) according to DIN 51385, as well as laws limiting their application.

Table 7: Limit values for metalworking components (excerpt)

NOXIOUS COMPOUNDS	LIMIT VALUES		THE LAW
	air, TRGS900	TZOM	
Secondary amines	-	≤ 0.2 % (concentrate)	TRGS 611
Barium (salts)	0.5 mg/m³	≤ 10 ppm (concentrate)	
Diethanolamine(2.2. iminodiethanolamine)	15 mg/m³	≤ 0.2 % (concentrate)	TRGS 611
Nitrite and compounds	-	prohibited ≤ 20 mg NO_3/l (emulsion, solution)	TRGS 611
Chloroparaffins (clorinealkanes)	-	≤ 0.2 %	The Waste Act and TRGS 905
PCB, PCT	1-0.5 mg/m³	≤ 4 ppm	The Waste Act
1,2-Benzoisothiasole-3(2H)-on		≤ 0.05 % (emulsion, solution)	25. ATP declare R 43 above 0.05 %
Benzo-α-pyrene (PAH/PAK)	0.002 mg/m³	50 ppm	21. ATP
1,3,5-tris-(2-Hydroxiethil)-hexadidro-1,3,5-triazine(HHT)		≤ 0.1 % (emulsion, solution)	25. ATP declare R 43 above 0.1 %
Aerosols and vapours	5 mg/l (air) 20 mg/l (emulsion)		

*(21. ATP EU Directive 96/65/EG of 11/10/1996.

25. ATP EU Directive 98/98/EG of 18/9/1998.

67/548/EWG - Dangerous Substance Directive, The Basic and Special Ones, of 16/8/1967.

TRGS 611 - Technische regeln fuer Gefahrstoffe "Limit values for water miscible metalworking fluids, if N-nitrozoamines May be Developed" 2/2000.

TRGS 905 – The List of Compounds which are Cancerogenous, Mutagenic, Teratogenic, 2/2000.)

Chlorine-Based Compounds

Chlorine compounds may still be found in application, but much less in Europe than in America. The European Union has – by its Directive ECC 793/93 – prohibited the application of chlorine compounds in metalworking and leather processing fluids. Replacement compounds are being sought instead. Chlorinated paraffins, widely applied and the best known EP additives in metalworking fluids, are still being manufactured in the USA, and the producers are powerful. They may be harmful during application and waste management. Namely, at high pressures and temperatures at contact surfaces, and at lower waste incineration regimes, hydrogen chloride and dioxins may develop. According to molecule size, chlorinated paraffins fall down in three groups: chlorinated paraffins with a short hydrocarbon chain; with medium and long chain. Table 8 presents the classification of chlorine paraffins and a framework chlorine content per respective molecule.

Table 8: Chlorinated paraffine grades and chlorine content

CHLORINATED PARAFFIN GRADE	CHAIN LENGTH	CHLORINE CONTENT, %				
short-chained	C10 - C13	< 40	40 - 49	50 - 59	60 - 69	>70
medium-chained	C14 - C17					
long-chained	C18 - C30					

Due to doubts about a too soon prohibition of applying chlorinated paraffin and the impossibility to find an adequate replacement of the said additive, the testing of its harmfulness in some applications has been intensified. Risk has been assessed associated with short-chained Cl-paraffins. Acute toxicity is very low, and liver damage has been assessed after repeated dosage. It has no effect on genetic, teratogenous, or reproductive properties. When examining cancerogeneity, those short-chained have proven positive on liver, thyroid gland, kidneys, while the long-chained are negative. It has no effect on skin. While testing the environmental impact, the result is the life reduction of water organisms. They have also shown the tendency towards bioaccumulation in shells.

Due to the high risik posed by chlorinated paraffins, their manufacturers, as well as some chemichals manufacturers and consumers, have developed a programme of special protection and control measures, as well as of chlorine-based product management.

The impact of lubricants on humans during application

When it comes to occupational diseases associated with handling lubricants, the most frequent are dermatitis and respiratory diseases. Dermatitis or skin disease appears in the following three forms: irritation, chronic dermatosis and alergy. It is a skin reaction as organism barrier in contact with the lubricant. Respiratory diseases (asthma, bronchitis) are the result of the activity of either oil mist or aerosol, generated in the plants due to increased temperatures, high speeds, and the like. Between the lubricant (mist, aerosol) and the respiratory system cell, there occurs a chemical reaction. Out of occupational dermatoses in the metal working industry, in Germany, 30-50% are the result of the contact with a metalworking fluid. It may be caused by the components of the fluid itself, but, more frequently, it is caused by pollution entering the fluid during operation. It may be “foreign” oil, microorganisms, tiny particles of metal and material from the tools, agents for workpiece conservation, cleaning agents, etc.

In order to evaluate the impact of componenats on people with problems, tests are performed using the following methods: Epicutaneous test, open and closed, Duhring Kammer test, Transepidermal tests, RBC test (red blood cell), BUS test (bovine udder system), etc. The tests are performed by authorized medical institutions.

Skin protection measures may be either medical or technical. A considerable part of the medical protection consists in early detection of the cause, essential for preventing future dermatoses. The skin protection plan encompasses the choice of skin protection agents, skin cleaning and care according to the specific conditions of the workplace. As regards technical measures, the most important is the prevention of contact, and then application of protective gear: suit, gloves, glasses, etc. Of particular importance is the choice of less health hazardous lubricants, as well as maintenance measures.

IMPACT OF WATER ON LUBRICANT QUALITY

Water content in lubricants which are mixed with water for preparation ranges from 85 to 98 %, and so it is understandable that the water impact is extremely high. They are lubricants applied for metalworking, in hydraulic systems; protection agents, rinsing and degreasing agents, and the like. Water may cause sludge formation, increase corrosion, destabilize product, increase microorganism growth, and the like.

Undesirable water impact is prevented by either chemical or physical methods. Water impact may chemically be neutralized by adding the so called “conditioner” into products or directly into water before application. In view of a lower environmental impact, advantage is given to physical methods. The best known methods of physical water preparation are ionic exchangers, ultrafiltration, reverse osmosis and distillation. Depending on the necessary capacity, water preparation is done discontinuously in tank, or continuously by building into watercourses. Water analysis must by all means be done before operation, and also during operation when water is used for topping up. The following properties are being tested: pH, hardness, conductivity, microorganism content, chlorine content, solid particles content, etc. The frequency of analyses depends on the kind of preparation and the necessary application.

Lubricant service life and analysis

The future development is based on the principle of nature's regenerative capacity, bearing in mind energy saving, conservation of natural resources, waste reduction, change of production society: avoiding product discharge due to abundance or new production. The achievement of these goals requires a change of habits and giving precedence to closed circular flows, product longevity, optimal use of resources, and the possibility of reusing before management. This means impacting the product's service life. That is why it is important to set a lubricant's service life. Degradation of lubricant properties i.e. wear degree during application or evaluation of the remaining service life is tested by various methods. Determining a lubricant's wear degree may be conducted through modelling or experimentally. Wear evaluation most frequently isn't unequivocal, which is why, in practice, various methods are used in combination. For this purpose, new methods are being developed, which will be simpler, because it is important to obtain data as soon as possible on the very application spot, which is very often in field. A common drawback of these methods is that they have not been standardized.

The wear mechanism of a tribological lubrication system consists in the wear of contact surfaces, and lubricant consumption. If there is wear of the contact surfaces, there are wear particles present. Grease wear (rheological grease wear) or wear of other lubricants is an irreversible change of their properties.

In order to evaluate the lubricant's remaining service life, classical methods are used, such as HPLC, FTIR, UV –spectroscopy, IPC, etc. These methods determine the oxidation degree, oil content, additive content, acid number, base number, viscosity change, and the like.

One among the new procedures is the Linear Sweep Voltametry method, LSV, developed by SKF ECR and Fluitc. It is an elecroanalytical method measuring voltage. The remaining additive reacts chemically with the reagent compound, with, in the solvent, mostly antioxidants being present: ZDTP, PANA, BHT. The advantage lies in the simplicity of the procedure: sampling, mixing with 5 ml of reagent, putting into the tester and measuring.

Only a small volume of the sample is needed (up to 200 mg), and there is no need to extract the oil phase using solvent. Since the device is mobile, it allows for *in situ* analysis. Since it is fast, the method is suitable for field tests, especially when it comes to automotive and railway lubricants, and the like.

BEQUIET TEST (SKF) or noise determination is the method for measuring vibration occurring due to the presence of particles. It is suitable for measuring lubricant quality, and also its purity, as well as property degradation. It is known that if the lubricant film thickness is below 1 μm any particle with a larger diameter obstructs peaceful operation of the tribosystem and causes noise. According to this method, greases have been classified into the following four grades:

1. *dirty* - particle hardness and size after contact leave permanent damage - noise increase and bearing service life reduction,
2. *noisy* - particle hardness and size which may damage bearing surface and which inrease noise
3. *clean* - particle hardness and size may cause certain vibration, but there is no permanent surface damage,
4. *quiet* - maximum purity level, the smallest particles, minimal vibration.

The first group very rarely includes fresh lubricant, because they are usually the lubricants in operation. The second group consists of only several greases on the market: based on thickener or solid lubricant (typical example - some Ca complex greases). The third group usually includes greases based on polyurea making agglomerates, but they do not cause damage. The fourth grade includes only several greases, based on Li soaps, for they provide fine structure, or those greases which are produced in pure atmosphere. This method may be used also in grease development through purity evaluation. The purpose is to produce as quiet a grease as possible with the least possible property degradation.

Ferrography is the method used to separate the material wear particles from the lubricating oil sample. Material particles, chipped from the operating surfaces of the tribosystem parts, are the result of the wear process activity.

Wear particles are isolated from the lubricant based on magnetic attraction using suitable permanent magnets. The ferrographic method has been confirmed as a succesful technique for supervising the condition of closed tribological systems (engines, gear boxes, and the like).

The role of individual subjects in lubricant application

Lubricant producers, as well as users, are equally responsible for application and service life extension. Producers must improve product formulations, which must be less harmful for human health and the environment, with as long a service life as possible, with as simple a care and maintenance as possible, and as simple a waste fluid management as possible. The producer provides recommendations for care and maintenance, takes care of the compatibility with other materials, and provides recommendations for lubricant choice. The users must implement the measures of caring for the fluid, the workspace, and the employees, prevent pollution during application, remove pollutants from the operating fluid, and manage it after operation. The consumer must ensure as good a maintenance as possible using structural interventions, such as building in auxiliary machine elements: centrifuge, separators, filters, water preparation devices, etc.

Lubricant manufacturers and consumers must employ joint efforts to apply and test lubricants and work on the development of modern formulations. Tests may last several years. Apart from obtaining the best formulation possible for certain application conditions, the purpose of joint tests are the recommendations for global application of a given lubricant on the part of the machinery or equipment manufacturer.

During their operation, both the metalworking fluids and other lubricants need to be controlled with the purpose of undertaking correction measures and obtaining satisfactory performances. The testing of operating fluid during application requires a plan, and - in dependence of the analysis extent - daily, weekly or monthly work. One must also set care and maintenance procedures: personal, as well as regarding machine and fluid, environment, and also protection means. If necessary, when correcting the working fluid, physical methods have precedence over those chemical. Figure 4 shows a mobile machine for cleaning metalworking fluids, thus considerably extending the fluids' service life. Maintenance needs to be planned before the very decision on the application is taken in the scope of a comprehensive management plan.

Maintenance in a modern company

Maintenance means impacting the service life of natural resources, lubricants, and gear. The basic maintenance purpose – as well as that of the company itself – is to upgrade business making and prevent any losses.

Modern maintenance must consist in a systematic, processed thinking and acting. The share of unplanned maintenance measures must equal zero.

As regards the basic maintenance strategies, along with that corrective and preventive, advantage is given to that predictive, or condition-based maintenance. Analysis of the equipment's condition may be obtained on application spot by building in sensors and online control. Analysis of the lubricant may be performed by gear manufacturers in the scope of their technical servicing, or else samples may be transported to specialized laboratories. Based on lubricant properties obtained through analysis, they are compared with permissible limits after which an intervention is done in the tribological system, if necessary. This may be changing or repairing the lubricant, tool sharpening, repairing gears by welding, and the like. This kind of maintenance reduces total maintenance costs, use of spare parts; saves the personnel's working hours, while at the same time improving the product quality. Development of sensor technique leads to proactive maintenance.

Computer technology and electronic information paths, as well as the development of modelling procedures, also enable new lubricant application technique. Thus, using database, a technique has been developed of monitoring the need for lubricants and providing recommendations for TFM (total fluid management); in Germany, the KUSI project, etc. The application of this technique leads to a reduced engagement on the part of the production company employees, but also a reduced need for personnel, which may prove disastrous for some companies.

Solid lubricants, coats and composites

The need for a lubricant to be applied at extremely high temperatures, radiation, vacuum, and other extreme surroundings and conditions, has lead to the development of applying a solid lubricant film on contact surfaces. Solid fuels have appeared towards the end of 1940, and are now applied also in various areas of industry, automobile industry, as well as military and aircraft industry. Common solid lubricants are molybdenum disulfide (MoS_2), graphite, polytertafluorethylene (PTFE), tungsten disulfide (WS_2), lead, etc. Molibdenum disulfide and graphite have a low friction coefficient and a high load carrying capacity. PTFE shows the lowest friction coefficient, but also a low load carrying capacity. Graphite is not allowed for application according to most military specifications, because it causes galvanic corrosion. It is also known that molibdenum disulfide may cause corrosion if applied where the operating temperatures exceed 350^0C. At this temperature, MoS_2 oxidizes and creates sulfuric acid. Corrosion may appear also in other operating conditions, which is why it is very important to know them in case of applying solid lubricants. They are applicable under conditions where the putting and retaining of conventional lubricant is problematic, where there is dust and pollutants, where the operating temperatures range from –67 do +93 ^{0}C, etc. Lead and antimony are replaced because, as heavy metals, they are considered health hazardous and classified as hazardous waste. Coats are materials with lubrication property, put upon the surface using some of the suitable methods. Recommended thickness is up to several micrometers. They are considered as the third part of the tribosystem.

Modern mechanical industry is faced with the challenge of increased performance requirements of the precise sliding components with minimal structural changes. This may be achieved by applying a thin cover film contributing to wear and friction reduction. They are DLC (diamond-like carbon), PVD (physical vapour deposition): TiAlN, CrAlN, ZrN, ZrC and others. They may be put upon construction materials, such as steel, aluminum alloys, titanium alloys, etc. The application covers precise hydraulic components, engines, transmissions, etc.

Composite materials, MMC (metal matrix composite) are used as replacement for metal. They have excellent properties, such as resistance to wear and corrosion, resistance to moisture; they are lighter than metals and easier to transport and manipulate. They also have environmental advantages through weight saving and speed of work. They are applied in automobile industry, paper industry, agriculture, metalworking, etc. The content of the solid lubricant particles changes the characteristics of the composite. Out of new materials, significant is the application also of the so called metal foams produced out of waste materials, having excellent mechanical properties and low weight.

Solid lubricant film, coats, composites, ceramics and modern materials applied in tribological systems, on working materials or on tools enable lubrication with a lower volume of conventional lubricant (MQL) and, in some cases, also dry lubrication (without a lubricant). Lubricant-free lubrication has its environmental advantages, as well as drawbacks. Dry lubrication, for instance, cannot resolve the taking away of particles or temperature and in these application cases liquid lubrication is still irreplaceable.

Conclusion

Health, occupational safety and environmental protection are the main development boosters at the beginning of the new millenium. To this end many compounds in wide application need to be replaced due to their hazard for either health or the environment. It is also necessary to apply base oils which are less harmful for both people and environment. The application of natural oils as additives and base oils shall in the future have a big advantage. If they cannot be replaced, safety requirements suggest that the content of noxious compounds be labelled, as well as instructions supplied before, during, and after use – when they are turned to waste.

In the future, as a contribution to sustainable development, lubricant consumption will decrease, along with waste generation. Waste management needs to be as simple as possible, while biodegradability is one among the basic requirements for future lubricants. Generally speaking, modern lubricants must meet increasing requirements, both safety-related and technical. With the development of modern technology and materials, the volume of the necessary lubricant is decreasing, often yielding to minimal or dry lubrication.

Lubricants have better quality, but their prices are also increasing. Lubricant application cannot be influenced by their prices alone. The choice and application of lubricants must encompass the entire management of the lubricant, from its formulation, production, application, testing, reuse possibilities – all the way to waste management. Apart from lubricant producers and users, product or waste distributors, as factors of future development we must also include the economic policy and legislation of a given country or union.

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