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PRAĆENJE SVOJSTAVA BIOSTABILNE EMULGIRAJUĆE POLUSINTETIČKE TEKUĆINE ZA OBRADBU METALA TIJEKOM PRIMJENE

Sažetak

Emulgirajuće tekućine za obradbu metala podložne su kontinuiranom razvoju s ciljem zadovoljenja sve strožih zahtjeva zaštite ljudi i okoliša te poboljšanja ekonomičnosti.

Većina uobičajenih komponenti koncentrata zamjenjuju se novim za okoliš i čovjeka manje štetnim komponentama. Od moderne radne emulzije zahtijeva se što dulji radni vijek uz što jednostavnije i ekonomičnije održavanje. Produljenje radnog vijeka emulzije smanjuje ukupnu količinu otpadne emulzije, potrebu za korištenjem pomoćnih sredstava, unapređuje industrijsku higijenu, smanjuje troškove zbrinjavanja i ukupne troškove te konačno poboljšava ukupno gospodarenje tekućinama. Pri tome proizvođači maziva imaju značajnu ulogu: od proizvodnje modernih tekućina do davanja preporuka za izbor, čišćenje sustava, njegu i održavanje emulzije tijekom primjene, njegu ljudi a isto tako i za zbrinjavanje rabljene emulzije.

Izborom tekućine biostabilnog tipa znatno se produžava radni vijek emulzije u odnosu na konvencionalne emulzije. Biostabilna emulzija tijekom primjene ne zahtijeva posebno održavanje mada je poznato da se poboljšanjem njege produžava radni vijek emulzija.

U radu su prikazani rezultati ispitivanja biostabilne emulzije manje štetne za okoliš i zdravlje ljudi tijekom primjene pri različitim operacijama obradbe metala u više obradbenih tvornica.

UVOD

Tekućine za obradbu metala koje se miješaju s vodom primjenjuju se pri različitim operacijama obradbe metala odvajanjem čestica za hlađenje, podmazivanje i ispiranje. Prvo svojstvo tekućina koje se miješaju s vodom je hlađenje što je rezultat sadržaja vode (više od 95%) koja ima najbolji koeficijent prijenosa topline. Drugo je podmazivanje koje je rezultat primjene pogodnog mineralnog ulja te aditiva. Osim toga tekućine služe za ispiranje metalnih čestica a isto tako i najfinijih čestica abraziva iz zone obradbe. Zbog prisutnosti vode i neprestanog stvaranja novih i stoga visoko aktivnih metalnih površina, tekućina također tijekom operacije obradbe osigurava privremenu zaštitu od korozije. Ciljevi primjene tekućina za hlađenje i podmazivanje su povećanje brzine obradbe i produktivnosti, postizanje željene kakvoće obrađene površine, smanjenje istrošenja alata te poboljšanje efikasnosti. Što veća efikasnost traži se i pri operacijama uz visoke brzine obradbe (HSO = high speed operation) koje su posljednjih petnaestak godina znatno unaprijedile obradbene procese (1). Stoga su tekućine važan faktor izrade troškova za cijeli postupak obradbe. Uz ove tehničke i ekonomske aspekte uporabe emulgirajućih tekućina za obradbu metala, valja dodati i aspekte uvjetovane sve većom brigom za zaštitu okoliša i zdravlja ljudi koji posljednjih godina postaju dominantni (2,3,4).

Briga o zaštiti okoliša odnosno zdravlja ljudi provodi se u više faza a to su: kemijski sastav formulacije, djelovanje na ljude i okoliš tijekom primjene, duljina radnog vijeka tekućine i, na kraju, zbrinjavanje. Proizvođači tekućina za obradbu metala vode brigu o smanjenju štetnosti kroz moderne formulacije svojih proizvoda koje zadovoljavaju najstrože zakonske norme ali i zahtjeve renomiranih potrošača ovih tekućina (5). Da bi se produljio radni vijek radnih tekućina, valja osigurati što bolje održavanje ili njegu i tekućine i radnog mjesta uključujući i djelatnike.

Razvoj tekućina za obradbu metala koje se miješaju s vodom

U primjeni postoji više vrsta tekućina za obradbu metala koje se miješaju s vodom i uglavnom se mogu svrstati u tri grupe što je prikazano u tablici 1. Proizvode se kao koncentrati a neposredno prije primjene miješaju se s vodom. Tekućine bez mineralnog ulja na osnovi sintetičkih komponenti pomiješanje s vodom daju otopine koje su prozirne. Tekućine s mineralnim uljem pomiješane s vodom daju emulzije. Emulzije su fino dispergirani sustavi ulja u vodi. Izgled emulzije ovisi o veličini čestica ulja i njihovoj raspodjeli u vodi. Što koncentrat tekućine za obradbu metala sadrži više ulja, dobivena emulzija je "gušća", odnosno čestice ulja su većeg promjera. Nasuprot tome, koncentrati s nižim sadržajem ulja daju prozirnije emulzije s manjim promjerom čestica. Polusintetičke tekućine daju poluprozirne emulzije a ako imaju biostatička svojstva, to su onda biostabilne emulzije. Za stabilnost i izgled emulzije odgovorna je vrsta i količina emulgatora a isto tako i vanjski faktori kao što su temperatura, kakvoća upotrijebljene vode, djelovanje mikroorganizama i slično.

Tablica 1: Vrste i sastav tekućina za obradbu metala koje se miješaju s vodom
Table 1: Types and composition of watermiscible metalworking fluids

VRSTA / TYPE	TIP I	TIP II	TIP III
Sastav Composition	na osnovi sintetičkih sirovina Synthetic feed-based	sadrže mineralno ulje With mineral oil content polusintetičke (biostabilne) semi-synthetic, (biostable)/	na osnovi mineralnog ulja Mineral oil-based konvencionalne conventional
Sadržaj mineralnog ulja, % Mineral oil content	0	20-40	60-70
AW/EP aditivi, %	do 15	do 15	do 15
Površinsko aktivne tvari, % Surface active substances	do 10	20-40	10-20
Korozijski inhibitori, % Corrosion inhibitors	15-40	5-40	5-15
Radni oblik/Working shape	otopine/Solutions	emulzije-mikroemulzije	emulzije-mliječne/Opaque
Veličina čestica, μm Particle size	0,01-0,1	0,1-1	1-10
Voda/Water, %	90-98	85-98	85-98

Da bi se zadovoljili djelomično suprotni zahtjevi, formulacije emulgirajućih ulja postaju sve složenije a zahtijevaju sve sofisticiranije komponente. U sastav koncentrata obvezatno ulazi uljna komponenta, emulgator i inhibitor korozije a prema potrebi i drugi spojevi s ciljem poboljšanja radnih svojstava.

Zabrana uporabe kemijskih komponenata koje se smatraju opasnima za zdravlje i okoliš znatno je utjecala na sastav tekućina za obradbu (6). Inicijative za poboljšanje sigurnosti pri radu i zaštite okoliša pri uporabi tekućina za obradbu metala počele su daleke 1965. g. smanjenjem sadržaja alkalnih spojeva odnosno reguliranjem pH vrijednosti. Sedamdesetih godina u formulacijama se zabranjuju nitriti, a osamdesetih se raspravlja o upitnoj primjeni cinka. Najznačajnija inicijativa je početak brojanja mikroorganizama u radnim emulzijama. Tada se pojavljuje pojam biostabilnosti i potreba razvitka biostabilnih formulacija. Rješenje je bila primjena spojeva borne kiseline koji su emulzijama znatno produžili radni vijek. Tijekom osamdesetih a osobito početkom devedesetih pojačane su inicijative za zabranom ili smanjenjem većine spojeva odnosno komponenti tekućina za obradbu metala kao što su aromatski spojevi, klorni spojevi, sekundarni amini i slično. (7) Zbog toga se upotrebljava bazno ulje s nižim sadržajem aromata, emulgatori bez aromatske jezgre, monoetanolamini i trietanolamini umjesto dietanolamina i slično. (8) Da bi se dobile lako biološki razgradljive tekućine, kao uljna komponenta mogu se primijeniti sintetička ulja (sintetički esteri). S ciljem poboljšanja stabilnosti emulzije, produženog radnog vijeka tekućine i fleksibilnosti prema novim formulacijama kao što su formulacije bez dušika i amina, eterkarboksilati su posljednjih godina postali najprimjenjivanijim dodatkom sustavima emulgatora.

Utjecaj mikroorganizama na tekućine za obradbu metala

Radne emulzije su pogodna hrana bakterijama jer sadrže masne kiseline, alkohole, estere i druge spojeve koji sadrže biogene elemente i to u vodenom mediju i na pogodnoj temperaturi. (9) Premda koncentrati uglavnom ne sadrže mikroorganizme, kontaminacija emulzija bakterijama, gljivicama i plijesnima ne može se izbjeći. Naime, sustavi s tekućinama za obradbu su otvoreni i stoga jako osjetljivi na okolnu atmosferu koja je puna mikroorganizama različitih vrsta. Mikroorganizmi mogu degradirati sastav tekućine za obradbu što dovodi do osiromašenja emulzije emulgatorom te i do raspada emulzije. (10) Poradi njihovog svojstva brzog razvoja niski broj od samo 100 jedinica u 1 ml može se razviti u roku od nekoliko sati u broj 10.000.000 u 1 ml što se vidi na slici 1. Produkti metabolizma mikroorganizama su primjerice organske kiseline koje smanjuju pH vrijednost i uzrokuju neugodan miris. Neadekvatna industrijska higijena i neinhibiran rast mikroorganizama mogu rezultirati stvaranjem biofilmova na stijenkama spremnika ili sustavima za filtriranje. Biofilm je kompleksan sustav prljavštine u kojemu mikroorganizmi grade optimalne životne uvjete i u kojem su zaštićeni od kemijskog i fizikalnog utjecaja. Debljina sloja biofilma može biti i do nekoliko centimetara. Ako se dio otkine, može uzrokovati zastoj stroja začepljenjem vodova tekućine. Biofilm je konstantan izvor zagađenja a prije svakog novog punjenja emulzije mora se provesti temeljito čišćenje i dezinfekcija.

Slika 1: Razmnožavanje mikroorganizama u satu

Figure 1: Multiplication of microorganisms in hours

Emulzije konvencionalnog tipa ili mliječne emulzije imaju kratak radni vijek, oko mjesec dana do najviše 3 mjeseca, upravo zbog izrazite pogodnosti za rast mikroorganizama. Da bi se spriječila razgradnja odnosno kvarenje emulzije, postoje dva rješenja. Prvo je dodatak baktericida i fungicida u koncentrat a drugo sastav tekućine koja nije pogodna za rast mikroorganizmima. Od velikog izbora spojeva s baktericidnim svojstvima, danas se traže oni koji su manje štetni za ljude i okoliš. Uporabom modernih polusintetičkih tekućina za obradbu metala na osnovi derivata borne kiseline smanjuje se potreba za dodavanjem baktericida. Naime, borati imaju prirodno svojstvo sprječavanja rasta mikroorganizama, odnosno biostatička svojstva iako se u novije vrijeme govori o potrebi zamjene boratne kemije. (11) Formulacije s biostatičkim svojstvima nazivaju se biostabilnim tekućinama za obradbu metala. Biostabilne emulzije imaju najmanje dvostruko dulji radni vijek od konvencionalnih emulzija.

Njega i održavanje tekućina za obradbu metala

U obradbenim tvornicama potrebno je organizirati službu za podmazivanje. Najčešće je briga o podmazivanju povjerena službi za održavanje u tvrtki iako postoje tendencije za izdvajanjem službi održavanja. Moderne tvrtke optimalizacijom održavanja poboljšavaju ekonomičnost. Cilj održavanja je postići proizvodnju bez zastoja odnosno proizoditi troškove koji se približavaju nuli.

Služba za podmazivanje mora, uz osnovno poznavanje tehnološkog procesa, biti informirana o kakvoći i primjeni svih maziva pa tako i tekućina za hlađenje i podmazivanje pri obradbi metala. Proizvođači maziva su dužni informirati potrošače o svim osobinama maziva: od sastava maziva, sigurnosti pri radu s tim mazivom te o uklanjanju kada postanu otpadne. S tim ciljem proizvođač daje različite upute, tehničke i sigurnosno-tehničke liste, te organizira obuke djelatnika putem seminara.

Proizvođač zajedno s potrošačem izrađuje plan podmazivanja, pomaže pri izboru odgovarajućeg maziva, radi planove ispitivanja i održavanja radne tekućine, a isto tako i preventivne zaštite i njege ljudi. Tijekom rada s mazivom, a također i s emulzijama valja slijediti savjete proizvođača čime se može izbjeći većina problema i osigurati dulji radni vijek emulzije. Nakon izbora odgovarajućeg maziva služba za podmazivanje mora voditi računa o kontinuitetu nabave, distribuciji do stroja, ispravnoj primjeni i postupanju nakon istrošenja.

Pri organizaciji podmazivanja i održavanja valja razmotriti postojeće stanje strojeva. (12) Naime, u obradbenim radionicama često se nalaze vrlo stari strojevi kojima pojedini dijelovi ne rade ili ih nema, primjerice filtri. Stoga je potrebno izvesti konstrukcijske preinake strojeva ali i njihovog okruženja. Tako se stalno kapanje "stranog" ulja može skupljati odvojenim spremnikom a prednost valja dati centralnom sustavu podmazivanja ako je to moguće. U strojevima s individualnim punjenjem radni vijek emulzije konvencionalnog tipa je oko pet tjedana. U centralnim sustavima podmazivanja ista emulzija može izdržati približno dvostruko duže i to bez posebne njege ili održavanja. Radni vijek emulzije može se produžiti ugradnjom potrebnih elemenata obradbenim strojevima, primjerice, uređaja za odvajanje stranog ulja ili skimera, magnetskih separatora i filtar-traka za uklanjanje metalnih čestica, brusnog materijala i dr. Ako se isparena voda nadoknadi demineraliziranom vodom, vijek emulzije se još jedanput udvostručuje što ukupno iznosi oko 40 tjedana rada. Slika 2 pokazuje kako produženje radnog vijeka emulzije smanjuje troškove koji se u ovome slučaju sastoje od troškova za materijal i troškova za rješavanje otpada.

Od koncentrata vodomješljive tekućine za obradbu metala pripremaju se radne emulzije najčešće koncentracije 2-10%. Koncentracija ovisi o zahtjevima dotične primjene. Radne emulzije spravljaju se u pogonima neposredno prije primjene i to ulijevanjem koncentrata u vodu mehanički. Emulzije se mogu spravljati i tzv. injektorima pri čemu valja paziti da ne radi na “prazno” što bi moglo uzrokovati upuhivanje zraka u vodu i dovesti do poremećaja ravnoteže emulzijskog sustava. Voda treba bakteriološki biti što čišća, neutralna i s određenom tvrdoćom. Najbolja je ona koja se koristi za piće dok se vode iz rijeka ili tehnološke vode ne preporučuju bez pročišćavanja. Valja naglasiti da su vode za piće obično tvrde vode koje zbog visokog sadržaja kalcija mogu stvarati kamenac a isparavanjem tijekom primjene sadržaj soli se povećava što onda smanjuje životni vijek tekućine. Zbog toga se mogu primijeniti neke od metoda omekšavanja vode primjerice ionskim izmjenjivačima, kemijskom obradbom i sl.

Slika 2: Utjecaj duljine radnog vijeka emulzije na troškove (Izvor: H.Kissler, ABAG Abfallberatungsagentur, Fallbach)
Figure 2: Influence of emulsion working time to the costs (Source: H.Kissler, ABAG Abfallberatungsagentur, Fallbach)

Tijekom primjene vodomješljivih tekućina za obradbu metala nekoliko faktora šteti stabilnosti emulzije i otopine i time smanjuju njihov radni vijek. To su: iscrpljenje aktivnih tvari, prisutnost nečistoća, dotok stranog ulja, sredstava za čišćenje i soli, napadaj mikroorganizama, isparavanje vode, prodori različitih tvrdoća vode i sl. Do iscrpljenja aktivnih tvari, osobito emulgatora, može doći potroškom u radu a zatim zbog djelovanja mikroorganizama i oksidacijom. Prisutnost nečistoća, primjerice čestica metala ili grafita pri obradbi sivog lijeva, čine sustav nestabilnim zato što imaju visoku adsorptivnost zbog njihove velike specifične površine a služe i kao nositelji za mikroorganizme. Strano ulje koje obično ulazi s vodilica i iz hidraulike stvara sloj na površini emulzije koji sprječava doticaj emulzije sa zrakom i na taj način osigurava anaerobnim bakterijama uvjete za razgradnju emulzije i pojavu neugodnog mirisa. Ovaj miris izraženiji ponedjeljkom ujutro rezultat je mikrobiološke razgradnje ili tzv. monday morning smell. Sloj stranog ulja može poslužiti i kao nosač mikroorganizama a osobito plijesni, te je zbog toga potrebno ulje s površine uklanjati redovito. Potrebno je osigurati miješanje emulzije tijekom mirovanja stroja zbog prozračivanja emulzije te stalno osvježavanje emulzije tijekom primjene. Često se prilikom izmjena punjenja radna emulzija zagadi sredstvima za čišćenje. Vode za spravljanje radnih emulzija obično su tvrde vode koje sadrže različite anione i katione. Ulazak elektrolita slabi djelotvornost emulgatora pri formiranju orijentiranog naelektriziranog sustava emulzije odnosno smanjuje stabilnost emulzije. Jačina utjecaja elektrolita je u nizu: anioni SO_4^{2-} > CH_3CO^{2-} > Cl^- > Br^- > NO_3^- > ClO_3^- te kationi Mg^{2+} > Ca^{2+} >Sr^{2+} > Ba^{2+} > Li^+ > Na^+ > K^+ itd. Tijekom dugotrajnog rada dolazi do povećanja koncentracije soli zbog isparavanja. Prema redoslijedu jakosti pojedinih iona očito je da se i njihove soli slično ponašaju. Tako je redoslijed najutjecajnijih soli na stabilnost emulzija slijedeći: $MgSO_4$ > Na_2SO_4 > $(NH_4)_2SO_4$.

Tablica 2. Plan analiza radne emulzije (Izvor: Ch. Kaulbery, AUDI AG, Ingolstadt)
Table 2: Working emulsion analyses plan (Source: Ch. Kaulbery, AUDI AG, Ingolstadt)

Svojstvo / Property	Učestalost ispitivanja/Testing frequency			Metoda
	1x tjedno weekly	2xmjeseč. monthly	1xmjeseč. monthly	
Izgled/Appearance	x			Vizualno/Visual
Miris/Odour	x			-
pH-vrijednost/pH value	x			Potenciometrijski/Using potentiometer
Stabilnost/Stability	x			Statički/Statical
Koncentracija/Concentration [%]	x			Refraktometrom/Using refractometer
Određivanje koncentracije stranog ulja/ Induced oil conc. determination [%]	X			Cijepanjem, titracija emulgatora/Splitting, Titration (DIN 51368)
Nitriti i nitrati, [mg/l]	x			Test trake/Ribbon test
Antikoroz. svojstva/Anti-corrosion propert.		x		DIN 51360/I i II
Vodljivost/Conductivity [μS/cm]		x		Mjerenjem otpora/Resistance meas.
Ukupna tvrdoća/Total hardness [^{0}nj]		x		Kompleksometrijski/Complexometric
Mikrobiol.slika/Microbiol.appearance [br/ml]			x	CS-/Sa agar, "dip slide"
Otpuštanje formald./Formaldehyde rel. [%]			x	Destil. vod. parom/Water vap. dist.
Kloridi/Chlorides [mg/l]			x	Titracija s /Titration with $AgNO_3$
Krute čestice/Solids [%]			x	Filtracija/Filtration

Malo je poznato da tvrdoća vode znatno utječe na rast mikroorganizama u radnim emulzijama. Najutjecajnije soli iz vode su kalcijev i magnezijev klorid te kalcijev i magnezijev karbonat u koncentraciji do 1500 ppm a iznad te vrijednosti imaju inhibirajuće djelovanje.

Osnovna primjenska svojstva radne tekućine potrebno je ocjenjivati svakodnevno a to su: razina otopine, miris, izgled i prodor ulja, nečistoća, korozijske pojave na stroju ali i na obradcima te lijepljenje i pjenjenje. Redovite analize za praćenje emulzija također su od velikog značenja. (13) Korisno je napraviti plan analiza kakav se, primjerice, primjenjuje u velikoj njemačkoj tvornici automobila (tablica 2).

EKSPERIMENTALNI DIO

Cilj ispitivanja

U radu se pokušalo u praksi ispitati radna svojstva biostabilne tekućine za hlađenje i podmazivanje pri različitim vrstama obradbi metala i u različitim tvornicama. Praćena su četiri sustava s radnim emulzijama definiranih koncentracija. Ciljevi su bili različiti i ovisni o zahtjevima sustava odnosno potrošača, od zadovoljenja kakvoće obrađene površine, dobrog ispiranja, zaštite od korozije pa do otpornosti prema mikrobiološkom zagađenju. U tablici 3 prikazani su obradbeni strojevi i uvjeti rada ispitnih emulzija, vrsta obrađivanog metala kao i zadano vrijeme eksploatacije.

Ispitna tekućina

Ispitna tekućina je polusintetička biostabilna emulgirajuća tekućina za obradbu metala koja je sastavljena prema najnovijim zahtjevima zaštite ljudi i okoliša u području obradbe metala. Ukupni sadržaj aromata je smanjen tako da je upotrijebljeno mineralno ulje parafinske osnove s niskim sadržajem aromata.

Umjesto derivata alkilbenzena, do sada najraširenije grupe emulgatora, upotrijebljena je smjesa prirodnih kiselina i derivata masnih kiselina. Kao korozijski inhibitor i regulator rasta mikrooganizama upotrijebljen je derivat borne kiseline. Ova formulacija ne sadrži spojeve klora, dietanolamina (DEA), nitrite, nitrate niti druge spojeve s tzv. negativne liste. Svojstva koncentrata i emulzije prikazani su u tablici 4.

Tablica 3: Pregled radnih emulzija i uvjeta rada obradbenih strojeva
Table 3: A rewiev of working emulsions and working conditions of machines

Radna emulzija Working emulsion	E1	E2	E3	E4
Obradbeni stroj Machine	Univerzalna brusilica - Universal grinding machine UFD 1000	Glodalica - Milling machine NC NORTE HS1	Honsberg linija, 16 strojeva - Honsberg line, 16 machines	Poluautomatska glodalica TOS, MFA 6 - Semi-automatic milling machine
Obradba Working type	brušenje, unutarnje i vanjsko - Grinding, internal and external	glodanje, bušenje, tokarenje - Milling, drilling, turning	duboko bušenje, glodanje, razvrtanje, brušenje - Deep drilling, milling, reaming, grinding	glodanje, izrada zupčanika - Milling, gear cutting
Metal koji se obrađuje Type of metal worked	čelik, sivi lijev - Steel, cast iron	čelik, silumin, alatni čelik, aluminij - Steel, silumine, tool steel, aluminum	sivi lijev - Cast iron	sivi lijev - Cast iron
Dodatna oprema Additional equipment	magnetni filtar - Magnetic filtre	mehanički transporter strugotine - Mechanical chip transporter	ciklon + transporter strugotine, aerator - Cyclone + chip transporter, aerator	usisavanje ulja s površine - Oil sucking in from the surface
Volumen emulzije, l Emulsion volume	350	120	11000	100
Miješanje emulzije Emulsion stirring	ručno, polugom (posuda 20l) - Manually, using a bar (20 l container)	ručno, polugom (posuda 20l) - Manually, using a bar (20 l container)	injektor, ciklon - Injector, cyclone	ručno, mlazom (posuda 20l) - Manually, by spla-shing (20 l container)
Koncentracija, % Concentration	2	5	4	4,5
Zadani zahtjevi Requirements set:	Dulji radni vijek emulzije, dobro ispiranje i hlađenje - Prolonged emulsion service life, good washing out and cooling	Dulji radni vijek emulzije i alata - Prolonged emulsion and tool service life	Dulji radni vijek emulzije, dobro ispiranje i hlađenje - Prolonged emulsion service life, good washing out and cooling	Dulji radni vijek emulzije i alata, kompatibilnost sa strojnim uljima-Prolonged emulsion and tool service life, compatibility with machinery oils
Zadani rok rada Set operation time	3 mj. - 3 months	3 mj. - 3 months	3 mj. - 3 months	3 mj. - 3 months
Ostvareno vrijeme rada Realized operation time	>12 mj. - >12 months	>12 mj. - >12 months	>12 mj. - >12 months	>18 mj. - >18 months

REZULTAT ISPITIVANJA I DISKUSIJA

Nova biostabilna emulgirajuća tekućina za obradbu metala ispitana je na više obradbenih strojeva u nekoliko tvornica. Emulzije za ispitivanje na pojedinim strojevima priređene su prema mogućnostima u tvornicama uglavnom ulijevanjem koncentrata u vodu. U tablici 5 prikazani su rezultati ispitivanja uzoraka radne emulzije na univerzalnoj brusilici UFD 1000 Kikinda. Ispitivanje je počelo krajem ljeta i trajalo je četiri mjeseca. Radno vrijeme emulzije je bilo kroz dvije smjene a stajanja su bila vikendom, po 2 dana i tijekom državnih praznika 5 do 10 dana. Uzorci su uzimani svaki tjedan u početku a kasnije dva puta mjesečno. Za operaciju brušenja primijenjena je koncentracija od 2%. Iz rezultata se vidi da koncentracija varira od 1,8 do 2,6% a ovisna je o odnošenju s obradcima i isparavanju te o nadolijevanju. Rezerve alkalija tijekom primjene padaju.

Tablica 4 Svojstva ispitne tekućine za obradbu metala
Table 4: Test metalworking fluid properties

SVOJSTVO PROPERTY	KONCENTRAT CONCENTRATE		METODE ISPITIVANJA TEST METHODS
Izgled i boja - Appearance and colour	bistro, žuto ulje - Clear, yellow oil		Vizualno - Visual
Stabilnost - Stabilty, 0 - 70^{0}C/24 h	stabilno - stable		Interni test 1
Viskoznost pri - Viscosity at 40^{0}C,mm^2/s	200		ISO 3104
Gustoća pri - Density at 20^{0}C, g/ml	1,02		ISO 3675
Emulzija (vodov. voda, 14^{0}nj) - Emulsion (tap water)	3 %	5 %	
Izgled i boja - Appearance and colour	poluprozirna, žućkasta - Semi-transpar., yellowish		Vizualno
Stabilnost - Stability, 20^{0}C/24 h	stabilna - Stable		Interni test 3
Rezerve alkalija - Alkali reserves, ml 0,1nHCl (R.a.)	4,3	11,5	ASTM D 1121
pH-Vrijednost - pH-value	9,12	9,23	ASTM D 1287
Korozijska svojstva - Corrosion properties 1,2 % emulzija 2 % emulzija	R0/S0 0		DIN 51360/I (Herbert) DIN 51360/II (Filtar papir)
Korozija prema obojenim metalima silumin, aluminij, bakar, mjed - Corrosion to non-ferrous metals silumine, aluminum, copper, brass	00		Interni test 11
Pjenjenje, volumen pjene - odmah, ml Foaming, foam volume -immediately -nakon 5 minuta-after 5 minutes, ml	35 0	40 0	Interni test 2
EP-svojstva - EP properties -Srednji promjer istrošenja - Mean wear scar, mm(S.p.i) -Površina istrošenja-Wear surface, mm^2 (P.i.)	0,87 32,0	0,85 30,5	ASTM D 4172 Reichertova vaga - R. balance

Budući da se metode određivanja koncentracija ne podudaraju, može se zaključiti da u emulziju ulazi strano ulje koje smeta pri mjerenju koncentracije refraktometrom povećavajući vrijednost. Određivanjem korozije vidi se da svojstva zaštite od korozije padaju što može biti uzrokovano smanjenom koncentracijom tekućine za hlađenje i podmazivanje, ulaskom stranog ulja, povećanjem koncentracije soli zbog isparavanja te djelomično radom mikroorganizama. Tijekom primjene broj mikroorganizama je nizak ali se pri kraju povećao čemu je uzrok velika koncentracija stranog ulja te finih čestica metala i brusnih materijala, odnosno manja stvarna koncentracija emulzije. Od uobičajenih sojeva mikroorganizama izolirane su samo aerobne mezofilne bakterije koje su pokazatelj ukupnog broja bakterija te plijesni. Osvježavanjem radne emulzije stanje se popravilo te je nastavljen rad i dalje (više od godinu dana). Prema izvješću djelatnika pri stroju nije bilo korozije, lijepljenja, neugodnog mirisa a niti reakcije na kožu ili dišne organe.

Tablica 5: Rezultat laboratorijskog ispitivanja uzoraka radne emulzije E1 (brusilica UFD 1000)
Table 5: Laboratory test results of working emulsion E1 samples (grinding machine UFD 1000)

Datum - Date	17.9	22.9	29.9	6.10	13.10	20.10	5.11	19.11	25.11	17.12	19.1.
Rad. dan-Workday	0	4	11	18	25	32	48	62	68	89	120
Izgled i boja Appearance,colour	*	**	**	***	***	***	***	***	***	****	****
pH vrijednost pH-value	8,97	9,07	8,90	8,94	9,02	8,89	8,94	8,95	8,94	8,74	8,74
R.a., ml 0,1nHCl	4,45	4,80	6,91	5,40	6,10	4,36	3,87	4,60	5,02	4,30	4,30
Konc.refr, %	1,8	1,9	2,4	2,2	2,6	1,9	2	2,2	2,2	2,0	2,0
Korozija-Corrosion -Herbert -Filtar test	 R0/S0 1	 R0/S0 1	 R0/S0 0	 R0/S0 0	 R0/S0 0	 R0/S0 1	 R0/S1 3	 R0/S0 2	 R0/S0 2	 R0/S1 4	 R0/S1 4
Pjenjenje-Foaming odmah-immed.,ml nakon-after 5',ml	 20 13	 20 0 (5s)	 25 0,5	 30 0	 25 0	 15 0	 10 0	 25 2	 20 4	 30 4	 30 4
S.p.i.. mm P.i., mm^2	0,56 25,1	- -	0,61 30,3	- -	0,65 27,4	0,63 26,5	0,89 23,5	1,03 26,8	0,95 27,2	- -	1,38 23,3
Ukupni br. bakter. Tot. bacter.no./ml Plijesni-Mould/ml	10 0	600 0	10 50	20 170	20 180	1620 420	218400 0 250	124830 0 3	- -	342000 0 1	123900 0 5
Tvrdoća vode- Water hardn.,^{o}nj	15,25	12,36	10,84	14,83						9,80	

*=poluprozirna, sivo-crne plivajuće čestice-semi-transparent, gray-black floating particles, **= poluprozirna, lagano zamućena-semi-transparent, slightly opaque, ***= poluprozirna, zamućeno zelenkasta-semi-transparent, opaquely greenish, ****= slabo prozirna, smeđe-bjelkasta-poorely transparent, brownish-whitish

U tablici 6 prikazani su rezultati ispitivanja uzoraka radne emulzije iz univerzalne poluautomatske glodalice NC Norte HS1. Zadana je i pripravljena koncentracija 5% jer se na ovom stroju različitim vrstama operacija obrađuju različite vrste metala od obojenih do alatnih čelika. Iz rezultata analize vidi se stabilnost pH vrijednosti koja je bila između 8,8 i 9,13.

Korozijska zaštita Herbert i filtar papir testovima potpuna je tijekom cijelog vremenskog razdoblja. Pjenjenje je u početku bilo veće zbog relativno niske tvrdoće vode, a tijekom vremena se smanjilo. Broj mikroorganizama se lagano povećava tijekom primjene ali ne prelazi 10^4.

Tablica 6: Rezultat laboratorijskog ispitivanja uzoraka radne emulzije E2 (NC Norte HS1)
Table 6: Laboratory test results of working emulsion E2 samples (NC Norte HS1)

Datum - Date	29.9.	6.10.	13.10.	20.10.	5.11.	19.11.	25.11.	17.12.	19.1.
Radni dan - Workday	0	7	14	21	37	51	57	79	110
Izgled, boja Appearance, colour	*	*	**	**	**	**	***	****	****
pH vrijednost-pH value	9,00	9,03	9,10	8,80	9,08	9,13	9,10	9,04	9,04
R.a., ml 0,1nHCl	12,01	12,42	15,85	16,29	11,39	13,73	9,76	7,03	8,3
Konc.ref, %	4,4	5	6	5,9	5,2	5,8	4,5	3,1	4,1
Sadržaj ulja-Oil content, %	2,5	2,9	3,6	3,8	2,8	3,8	3,3	1,6	2,5
Korozija-Corrosion Herbert test Filtar test	R0/S0 0								
Pjenjenje-Foaming odmah-immediat., ml nakon-after 5', ml	50 46	40 30	40 33	43 26	43 22	38 32	35 28	35 2	30 5
S.p.i, mm P.i.,mm^2	0,80 25,8	- -	0,66 20,7	0,75 18,1	0,69 23,9	0,65 20,8	0,64 24,3	0,66 29,3	- -
Ukupni broj bakterija-Total bacteria no./ml Plijesni-Mould/ml	10 0	200 <10	140 10	1200 0	1000 240	6750 2	- -	2200 1	1265 0
Tvrdoća vode-Water hardness,°nj	10,84	14,83						9,8	12,5

*= poluprozirna, zamućena zelenkasta-semi-transparent, opaquely greenish, **= poluprozirna, zamućena smeđkasta-semi-transparent, opaquely brownish, ***= poluprozirna, zamućena zelenkasto-smeđa-semi-transparent, opaquely greenish-brownish, poluprozirna, zelena-semi-transparent, green

Tijekom rada u emulziju ulazi ulje s kliznih staza koje svojom prisutnošću povećava koncentraciju pri mjerenju refraktometrom. To se vidi i iz laboratorijskih analiza. Usporedbom koncentracija izračunatih trima metodama: preko određivanja sadržaja ulja cijepanjem kiselinom, rezerva alkalija i refraktometrom vidi se razmimoilaženje koncentracija, slika 3. Rezerve alkalija najbolje pokazuju stvarnu koncentraciju. U dva slučaja je koncentracija određena cijepanjem kiselinom niža od koncentracije refraktometrom, 37. i 79. radnog dana, što je posljedica odnosno pokazatelj uklanjanja ulja s površine emulzije industrijskom vakuum crpkom.

Emulzija E3 primjenjuje se u centralnom sustavu opskrbe emulzijom Honsberg pri obradbi kućišta motora od sivog lijeva. Ukupno je povezano sustavom podmazivanja 16 strojeva na kojima se rade pojedini stupnjevi proizvodnje kućišta od glodanja stranica, brušenja, bušenja, dubokog bušenja, kosog bušenja do honanja. Nastale čestice ispiru se emulzijom te odlaze u spremnik emulzije koji sadrži 11000 litara emulzije. Tu se kontinuirano izvlače metalne čestice mehaničkim transporterom uz izdvajanje finijih čestica ciklonima. Emulzija se kontinuirano miješa i protiče kanalima. U spremniku je konstruirano i prozračivanje emulzije.

Slika 3: Koncentracija rednih emulzija E2 određivana različitim metodama
Figure 3: E2 working emulsions concentration determined through various methods

Ovaj sustav je opterećen prodorom stranog ulja puknućima cijevi ali i s kliznih staza te bi valjalo ugraditi separator ulja pa bi se radni vijek emulzije produžio. Za sada se ulje skuplja crpkama. Pri pojedinačnim strojevima djelatnici rade s rukavicama ponajprije zbog velikih i oštrih strugotina što poboljšava njegu emulzije i higijenu ljudi. Rezultati ispitivanja ispitne emulzije E3 tijekom primjene u centralnom sustavu prikazani su u tablici 7. Zadano vrijeme ispitivanja bilo je tri mjeseca. Iz rezultata je vidljivo da dolazi do konstantnog povećanja koncentracije mjerenjem refraktometrom a isto tako i cijepanjem kiselinom dok rezerve alkalija ostaju konstantne. Neslaganje određivanja koncentracija različitim metodama ukazuje na prisutnost zagađivala a u ovom slučaju to je strano ulje. Uzrok ulaska ulja je jače curenje hidrauličkog ulja s jednog od strojeva. Kako sva emulzija kanalima i cijevima odlazi u zajednički spremnik tako i ulje zagađuje cijelu količinu emulzije. Vrijednost pH je uglavnom bila konstantna uz jednu iznimku i to devedeset petog radnog dana kada je pala. Uzrok pada pH vrijednosti je povećana mikrobiološka aktivnost. Zamiječene su naslage na rubu spremnika u cjevovodima i filtrima. Mikrobiološkom analizom utvrdili smo da su naslage nastale djelovanjem plijesni Acremonia kojih je bilo 1500 u 1ml (14). Razvoju ovih plijesni, čije su spore jako otporne i mogu dulje preživjeti u jako nepovoljnim uvjetima, pogodovala je visoka ljetna temperatura, mirovanje tijekom godišnjeg odmora, mala količina bakterija pa i prisutna dodatna hrana dotokom stranog ulja. Tom prilikom nije bilo kemijske intervencije već su se samo mehanički čistile naslage. Nakon čišćenja emulzija je normalno radila.

Tablica 7: Rezultat laboratorijskog ispitivanja uzoraka radne emulzije E3 (Honsberg)
Table 7: Laboratory test results of working emulsion E3 samples (Honsberg)

Datum - Date	20.5	28.5	3.6	15.6	23.6	2.7	10.7	14.7	21.7	30.7	4.8	27.8	18.9
Radni dan-Workday	0	7	12	24	32	41	48	52	59	67	72	95	117
Izgled, boja Appearance, colour	1	1+	1	1+	2	3	4	5	6			7	8
pH vrijednost-pH value	9,28	9,31	9,20	9,23	9,14	9,08	9,93	9,07	9,01	9,02	9,05	8,08	9,02
R.a., ml 0,1nHCl	8,24	8,24	8,72	8,03	9,41	9,03	9,67	8,79	8,65	8,55	10,5	7,40	8,10
Konc.refr.%	3,4	3,8	3,6	4,0	4,6	4,8	5,2	5,0	5,2	5,4	5,7	5,6	5,2
Sad. ulja,Oil content%	2,45	-	1,15	2,73	2,95	2,4	-	3,85	3,95	4,0	3,8	3,8	3,7
Korozija-Corrosion -Herbert test -Filter test	R0/S0 0												
Pjenjenje-Foaming odmah-immediat., ml nakon-after 5', ml	43 37	40 21	48 6	38 7	40 5	35 10	30 10	35 2	30 2	25 0	30 2	24 3	20 0
S.p.i., mm P.i., mm^2	0,64 30,1	- -	- -	- -	- -	0,65 34,3	- -	0,64 30,5	- -	- -	- -	- -	- -
Ukupni broj bakterija- Total bacteria no./ml	0	0	0	0	0	0	0	0	0	0	0	0*	0
Tvrdoća vode-Water hardness,°nj			7,09						7,54				

Izgled i boja: 1=zamućeno-zelenkasto, 1+ = 1+plivajuće čestice, 2 = mutno zeleno-smeđe, 3 = prljavo-siva, 4 = krem + plivajuće ulje, 5 = krem, sivo-smeđa, 6 = prljavo zeleno-siva, 7 = siva, 8 = krem boje.
Ukupni broj bakterija i enterobaktrija u 1 ml emulzije (Milk-bact trake) 24 i 48 sati: 0 = nema promjene na trakama, * = plijesni (72 h)
Appearance and colour: 1 = opaquely greenish, 1 + = 1+floating particles, 2 = opaquely green-brown, 3 = dark grey, 4 = cream + floating oil, 5 = cream, grey-brown, 6 = dark green-grey, 7 = gray, 8 = cream
The total number of bacteria and enterobacteria in 1 ml of emulsion (Milk-bact ribbons) for 24 and 48 hrs respectively: 0 = no change at the ribbons, * = mould (72 hrs)

U tablici 8 prikazani su rezultati ispitivanja uzoraka radne emulzije E4 s poluautomatske glodalice TOS MFA 6. Na stroju se operacijom glodanja urezuju zupci stalka dizalice. Stalak ima 28 zubi, modul 7 a dubina im je

15,3 mm. Okretni stol se vrti brzinom 63 u minuti a nož 84 u minuti uz posmak 0,96 mm u minuti. Uobičajeno je oštrenje noževa na stroju za oštrenje nakon 18 obrađenih komada a prilikom primjene ove emulzije razdoblje između oštrenja se produljilo. Rad stroja u proizvodnom procesu teče u tri smjene. U radnu emulziju konstantno ulazi ulje iz pogonskog reduktora te je potrebno češće uklanjanje plivajućeg ulja.

Tablica 8: Rezultati laboratorijske analize uzoraka radne emulzije E4 (glodalica TOS, MFA 6)
Table 8: Laboratory test results of working emulsion E4 samples (milling machine TOS)

Datum - Date	20.8.	24.8.	27.8	3.9.	9.9.	1.10.	4.2.	31.8.	14.10.
Radni dan - Workday	0	4	7	14	10	42	165	375	429
Izgled, boja-Appear., colour	*	**	**	***	***	***	****	****	***
pH vrijednost-pH-value	9,37	9,32	9,20	9,06	9,09	9,1	9,25	9,07	9,25
R.a., ml 0,1nHCl	8,51	10,08	9,19	10,9	8,8	9,2	9,65	15	15,73
Konc.refr. %	4,0	4,2	5,1	6,0	4,4	4,6	6,9	5,8	6,9
Korozija-Corrosion Herbert test Filtar test	 R0/S0 0	 R0/S0 0	 R0/S0 0	 R0/S0 0	 R0/S0 0	 R0/S0 0	 R0/S1 0	 R0/S0 0	 R0/S0 0
Pjenjenje-Foaming odmah-immediately, ml nakon-after 5',ml	 0 -	 0 -	 0 -	 24 3	 15 1	 20 1	 0 0	 0 -	 38 15
S.p.i, mm	0,85	-	-	-	-	0,97	0,75	0,64	-
P.i., mm^2	33,4	-	-	-	-	24,2	26,2	30,5	-
Ukupni broj bakterija- Total bacteria no./ml Plijesni-Mould /1ml	<100 10	<100 10	40 60	<100 <10	- -	<100 1	< 10^3 100	10^3 < 10^3	<10^3 <10^3
Tvrdoća vode-Water hardness,°nj	12,79		7,09						

*= polutransparentna žućkasta, lagano zamućena - semi-transparent, yellowish, slightly opaque, **= polutransparentna žućkasta, jače zamućena - semi-transparent, yellowish, more opaque, ***= neprozirna, žuto-smeđkasta - non-transparent, yellowish-brownish, ***= neprozirna, svijetlosmeđa - non-transparent, light brown

Mikrobiološkom analizom ispitana je otpornost radnih emulzija na razvoj mikroorganizama iz okoline. Određivano je devet vrsta mikroorganizama kako je prikazano u tablici 9. Od svih vrsta izolirane su samo dvije a to su plijesni te aerobne mezofilne bakterije koje su pokazatelj ukupnog broja bakterija. Broj mikroorganizama u uzorcima emulzije E4 je znatno niži od 10^4 što se smatra normalnom populacijom u biostabilnim tekućinama. Valja naglasiti da je u emulziji (drugog proizvođača) iz prethodnog punjenja glodalice MFA 6 izolirana Pseudomonas aeruginosa i to 100.000 kolonija u jednom mililitru. Emulzija je imala neugodan miris kojeg je uzrokovala upravo ta bakterija koja, osim toga, štetno djeluje na oči i kožu ljudi (uzorak emulzije od 19.8.) Na kraju zadanog radnog razdoblja emulzija određen je ukupni broj mikroorganizama koji se kreće oko vrijednosti 10^4 što se smatra zadovoljavajućim za biostabilne emulzije (tablica 10). Vidljivo je da su u sve četiri radne emulzije prisutne plijesni i gljivice dok bakterije nisu izolirane niti u jednoj emulziji.

Tablica 9: Rezultati mikrobiološke analize uzoraka radne emulzije E4 (glodalica TOS, MFA 6)
Table 9: Microbiological analysis results of E4 working emulsion samples (milling machine TOS, MFA 6)

Datum uzorkovanja emulzije Emulsion sampling date MIKROORGANIZMI, broj/1 ml	19.8. (preth)	20.8.	24.8.	27.8	3.9.	9.9.	1.10.	4.2.	31.8.
Salmonellae	0	0	0	0	0	0	0	0	0
Koagulaza (+) Staphylococcus	0	0	0	0	0	0	0	0	0
Sulphitoreducirajuće clostridiae	0	0	0	0	0	0	0	0	0
Proteus spp.	0	0	0	0	0	0	0	0	0
Pseudomonas aeruginosa	$1x10^5$	0	0	0	0	0	0	0	0
Enterococcus	0	0	0	0	0	0	0	0	0
Acremonium a. pl.	0	0	0	0	0	0	0	0	0
Aerobne mezofilne bakterije*	1,5 $x10^6$	89	90	40	80	90	80	100	1000
Plijesni - Mould	4200	10	10	60	10	1	20	10	<100

* = Ukupni broj mikrorganizama u 1ml emulzije - Total no. of microorganisms in 1 ml of emulsion

U emulziji E3 specijalna vrsta plijesni izolirana je upravo nakon zadanog vremena od tri mjeseca. Mehaničkim čišćenjem naslaga i dodatkom svježe emulzije nije bilo daljneg rasta. Može se zaključiti da nova emulgirajuća tekućina ukupni broj bakterija drži nisko a patogene vrste koje i uđu u emulziju ubrzo stagniraju rastom i na koncu ugibaju.

Tablica 10: Mikrobiološka slika radnih emulzija na kraju ispitnog razdoblja
Table 10: Microbiological rewiew of working emulsions at the end of experiment time

MIKROORGANIZMI	E1	E2	E3	E4
Koagulaza (+) Staphylococcus	0	0	0	0
Salmonellae	0	0	0	0
Enterococcus	0	0	0	0
Proteus spp.	0	0	0	0
Sulphitoreducirajuće clostridiae	0	0	0	0
Pseudomonas aeruginosa	0	0	0	0
Plijesni i gljivice - Moulds and fungi	+	+	+	+

Acremonium a. pl.	0	0	0*	0
Ukupni broj mikrorganizama u 1ml emulzije Total number of microorganisms in	3 x10^4	4 x 10^2	6 x 10^4	< 10^2
Koncentracija, % refraktometrom	1,8	5,0	5,2	4,0

0 = ne sadrži, + = sadrži,*) - tijekom ljeta nakupine, uklonjene mehanički-čišćenje
0 = does not contain, + = contains,**) - deposits acquired in summertime, removed mechanically - through cleaning

Korozijska svojstva radnih emulzija ostala su dosta dobra i nakon dugog razdoblja rada što se vidi u tablici 11. Ova emulzija ponajprije je formulirana za obradbu željeznih materijala te se određivanjem korozije metodama Herbert i filtar papir testom vidi njezina jako dobra antikorozijska zaštita i nakon duljeg razdoblja eksploatacije. Za dobru zaštitu od korozije obojenih metala potrebna je koncentracija veća od 2% što se vidi kod emulzije E1 koja ima koncentraciju 1,8%. U emulziji E3 prisutna je velika količina stranog ulja te nema dobru zaštitu mjedi.

Tablica 11: Rezultati laboratorijske analize svojstava zaštite od korozije radnih emulzija na kraju ispitnog vremena
Table 11: The results of anticorrosion properties examination of working emulsions at the end of the experiment time

METODA ISPITIVANJA - TEST METHOD	E1	E2	E3	E4
Herbert test, Fe-če, DIN 51360/1	R0/S0	R0/S0	R0/S0	R0/S0
Filtar papir test, Fe, DIN 51360/2	0	0	0	0
Korozija, aluminij, Interni test 11 Corrosion, aluminum, Internal test 11	+	0	0	0
Korozija, silumin, Interni test 11 Corrosion, silumine, Internal test 11	+	0	0	0
Korozija, mjed, Interni test 11 Corrosion, brass, Internal test 11	+	0	+	0
Koncentracija, % refraktometrom	1,8	5,0	5,2*	4,0

0 = nema korozije, + = korozija-zatamnjenje površne,*) stvarna koncentracija 3% - velik ulaz strojnog ulja
0 = no corrosion, + = corrosion - darkened surface,*) real concentration 3% - major machine oil penetration

Temeljem rezultata ispitivanja radnih emulzija i na osnovi iskustava u pogonima tvornica možemo reći da je formulacija biostabilne emulzije davala dobra svojstva hlađenja, zaštite od korozije, otpornosti prema mikroorganizmima ali i izvanredna maziva svojstva. Zbog polutransparentnog izgleda radne emulzije su omogućavale bolju preglednost zone obradbe. U proizvođačkim pogonima emulzije nisu stvarale neugodan miris, nisu uzrokovale lijepljenje strojeva niti skidanje boje. Emulzije nisu izazivale alergijske pojave kod radnika kao što su dermatološka oboljenja ili dišni problemi. Nije bilo potrebe za dodatkom kemijskih sredstava kao što su antipjenušavci, baktericidi ili fungicidi. Sve emulzije nastavile su daljnji rad a neke su u strojevima i preko godinu dana.

Zbog konstantnog odnošenja dijela emulzije sa česticama metala, obradcima a i zbog stalno prisutnog isparavanja vode povremeno je nadolijevana svježa emulzija niže ili više koncentracije ovisno o tome da li se ugušćuje ili razrjeđuje tijekom proizvodnog procesa. Neki pogoni imaju organizirane korekcije radne emulzije tjedno a neki svakodnevno, ovisno o već postojećim navikama održavatelja u tvornicama ili djelatnika pri strojevima. U slučajevima prevelikog ulaska ulja, Norte i MFA 6, ulje je uklanjano industrijskim vakuum crpkama prema potrebi. Ovo je specijalna formulacija namijenjena obradbi željeznih materijala. Zbog pažljivo odabrane smjese korozijskih inhibitora može se primijeniti i za obojene metale što je potvrđeno različitim vrstama operacija na tokarilici NORTE pri obradbi aluminija i drugih materijala.

ZAKLJUČAK

Brizi o sigurnosti pri radu i zaštiti okoliša daje se sve veća važnost u odnosu na postojeće tehničke zahtjeve. Sigurnost i zaštita okoliša imaju velik utjecaj na razvitak sirovina, na formulacije odnosno na proizvođače tekućina za obradbu metala.

U ovome radu prikazali smo primjenska svojstva nove tekućine za obradbu metala. To je polusintetička emulgirajuća tekućina koja s vodom daje biostabilne emulzije a svojim sastavom zadovoljava moderne zahtjeve sigurnosti pri radu i utjecaja na okoliš. Ova biostabilna emulzija u svim operacijama obradbe zadovoljila je zadane zahtjeve od hlađenja, podmazivanja i ispiranja do neutralnosti prema djelatnicima i otpornosti na rast mikroorganizama. U svim sustavima zadovoljila je zadani rok od tri mjeseca te nastavila raditi dulje od godine dana bez problema. Dugom radnom vijeku ove biostabilne emulzije pomoglo je i održavanje koje se provodi u pojedinim tvornicama.

Primjenom nove biostabilne emulzije unaprijedila se industrijska higijena, smanjila se količina otpadne emulzije, smanjili su se i ukupni troškovi, što sve doprinosi “ukupnom gospodarenju tekućinama”.

MONITORING THE PROPERTIES OF BIOSTABLE EMULSIFYING SEMI-SYNTHETIC METALWORKING FLUID AT APPLICATION

Abstract

Emulsifying metalworking fluids are subject to continuous development, with the purpose of meeting increasingly stringent human health and environmental protection requirements, as well as cost efectiveness advancement.

Most of the usual concentrate components are being replaced by new ones - less harmful for human health and the environment. A modern working emulsion is required to have as long a service life as possible, with as simple and as cost effective maintenance as possible. Prolongation of the emulsion's service life reduces the total quantity of waste emulsion, the need to use auxiliary means, promotes industrial hygiene, cuts down management costs, as well as overall costs, and finally advances fluid management in general. Lubricant manufacturers play an important role here: From the generation of modern fluids, to providing recommendations for the choice, system cleaning, emulsion maintenance at application, human care, and also for the used emulsion management.

The selection of a biostable fluid considerably prolongs the emulsion's service life with regard to conventional emulsions. At application, biostable emulsions do not require special maintenance, although it is well-known that improved care extends emulsion service life.

The paper provides results of testing a less human health and environmentally harmful biostable emulsion at application in various metalworking operations at several metalworking plants.

INTRODUCTION

Water-miscible metalworking fluids are applied for cooling, lubrication, and washing out in various metalcutting operations. The first feature of water-miscible fluids is cooling, resulting from the water content (over 95%), having the best heat transfer coefficient. The second is lubrication, resulting from the application of a suitable mineral oil, as well as additives. Apart from that, fluids are used for the washing out of metal particles, and also of the finest abrasive particles from the metalworking zone. Due to the presence of water and a continuous creation of new and hence highly active metal surfaces, during metalworking operations, the fluid also ensures a temporary corrosion protection. The goals of applying cooling and lubrication fluids are the increase of metalworking speed and productivity, achieving the desired quality of the metalworked surface, reduction of tool wear, and efficiency improvement. As high efficacy as possible is also required for HSO (high speed operations), which have considerably advanced metalworking processes over the past around fifteen years (1). That is why fluids constitute an important element in the calculation of the entire metalworking process costs. To these technical and economical aspects of using emulsifying metalworking fluids, we should also add aspects conditioned by the increasing human health and environmental concerns, dominating over the past years (2,3,4).

Human health i.e. environmental care is being implemented in several phases, as follows: The formulation's chemical composition, human health and environmental impacts at application, the fluid's service life, and, finally, the management. Manufacturers of metalworking fluids take care of reducing their noxious character through modern formulations of their products, meeting the most stringent legal standards, but also the requirements of their prominent users (5). In order to prolong the metalworking fluids' service life, it is necessary to ensure as good a maintenance or care of both the fluid and the workplace, including, of course, also the employees.

Development of Water-Miscible Metalworking Fluids

There are several water-miscible metalworking fluids in application. They may be more or less broken down into three basic groups, as shown in Table 1. Produced as concentrates, they are mixed with water just before application. Fluids without mineral oil content, based on synthetic components, when mixed with water, provide transparent solutions. Fluids with mineral oil content, based on synthetic components, when mixed with water, provide emulsions. Emulsions are finely dispersed systems of oil in water. The emulsion's appearance is dependent on the size of the oil particles and their distribution in water. The more oil the metalworking fluid concentrate contains, the "thicker" the emulsion obtained i.e. the bigger the oil particles' diameter. On the other hand, concentrates with lower oil content provide more transparent emulsions, with lower particle diameters. Semi-synthetic fluids yield semi-transparent emulsions. If they have biostatic properties, they are biostable emulsions. Emulsion stability and appearance is dependent on the emulsifyer type and quantity, as well as on external factors, such as temperature, the used water quality, microorganism activity, and the like. In order to meet the partially opposing demands, the emulsifying oil formulations are becoming increasingly complex, requiring more and more sophisticated components. Concentrate composition always as a rule includes oil component, emulsifier, and corrosion inhibitor, with, if necessary, other compounds, intended to advance its performances.

Prohibition to use chemical components which are considered hazardous for human health and the environment has had a considerable impact on the composition of metalworking fluids (6). Initiatives to advance occupational safety and environmental protection when using metalworking fluids date as far back as 1965, through the reduction of alkaline compounds content i.e. the pH value regulation. Nitrites were forbidden in formulations in the 70's, while the 80's brought about uncertainties as to whether zinc should be used. The most significant initiative was the beginning of counting microorganisms in working emulsions. That is when the notion of biostability appeared, along with the need to develop biostable formulations. The solution was to apply the boric acid compounds which have considerably extended the service life of emulsions. In the 80's, and especially towards the beginning of the 90's, initiatives were strengthened to prohibit or at least reduce the content of most metalworking fluid compounds i.e. components, such as aromatic compounds, chlorine compounds, secondary amines, and the like (7). That is why base oils were used with lower aromatic content, emulsifiers without aromatic rings, monoethanolamines and triethanolamines instead of diethanolamines, and the like (8). In order to come up with readily biodegradable fluids, synthetic oils (synthetic esters) may be applied as the oil component. In order to improve emulsion stability, prolong the fluid's service life, and achieve flexibility towards new formulations, such as nitrogen- and amine-free formulations, etherocarboxylates have, over the past few years, become the most applied addition to emulsifier systems.

Microorganism Influence on Metalworking Fluids

Working emulsions make a suitable food for bacteria, since they contain fatty acids, alcohols, esters, and other compounds containing biogenic elements in a water medium and at a favourable temperature (9). Although concentrates mostly do not contain microorganisms, emulsion contamination with bacteria, fungi, and mould cannot be avoided. Namely, metalworking fluid systems are open and therefore highly sensitive to the surrounding atmosphere full of microorganisms of various kinds. Microorganisms may degrade metalworking fluid composition, thus leading to the emulsion's emulsifier content reduction, and, eventually, its disintegration (10). Due to their fast development property, low number of merely 100 units in 1 ml may evolve within only several hours into 10000,000 in 1 ml, as shown in Figure 1. Microorganism metabolism products are, for instance, organic acids, lowering pH-value and causing unpleasant odour. Improper industrial hygiene and uninhibited microorganism growth may result in the generation of bio-films on the reservoir walls or the filtering systems. The bio-film is a complex system of dirt in which microorganisms are building optimum living conditions and in which they are protected from both chemical and physical influence. The bio-film layer thickness may be up to several centimeters. If a part of it is taken off, it may cause machine standstill by clogging the fittings through which fluid is supposed to pass. The bio-film is a constant pollution source. That is why each new emulsion fill must be preceded by thorough cleaning and disinfection.

Conventional or opaque emulsions have a short service life (around one month up to 3 months at the most) precisely because microorganisms are so very prone to their particular composition. There are two solutions available in order to prevent emulsion disintegration i.e. spoiling. The first one is the addition of bactericides and fungicides into the concentrate, and the other one is the fluid's composition which is not favourable for microorganism growth. Out of a wide selection of compounds with bactericide properties, the ones sought today are those less human health & environmentally harmful. The use of modern semi-synthetic metalworking fluids besed on boric acid derivatives has reduced the need to add bactericides. Namely, borates have a natural property of preventing microorganism growth, i.e. biostatic properties, although there has been talk lately of the need to replace the boric chemistry (11). Formulations with bio-static properties are called biostable metalworking fluids. Biostable emulsions have at least a doubly long service life than conventional emulsions.

The Care and Maintenance of Metalworking Fluids

Processing plants need to include lubrication services. The care of lubrication is most frequently entrusted to the maintenance department of the company itself, although there are also tendencies for their isolation. Modern companies increase cost efectiveness through maintenance optimization. The purpose of maintenance is to achieve production unhindered by standstills i.e. to produce costs equalling zero.

The lubrication service must, apart from some basic knowledge of the tecnological process, also be informed of the quality and application of all lubricants, including metalworking coolants and lubricants. Lubricant manufacturers must inform the consumers of all lubricant aspects: From lubricant composition, safety involved in handling it, and waste management matters. To this end, the manufacturer provides various guidelines, technical and safety/technical lists, as well as organizes employee training through seminars. Together with the consumer, the manufacturer draws up a lubrication plan, helps choose the adequate lubricant, elaborates the working fluid test and maintenance plans, as well as those referring to human preventative protection and care. While handling lubricants, and also emulsions, their manufacturer should be contacted, thus avoiding most problems and ensuring longer emulsion service life. After choosing the proper lubricant, the lubrication service must take care of a continued supply, distribution to the machinery, proper application, and handling after use.

While organizing lubrication and maintenance, one must consider the existing state of the machinery (12). Namely, metalworking workshops are frequently equipped with older machines, with some parts not working or even missing - such as filtres, for instance. That is why certain design changes need to be made involving the machines themselves, but also their surroundings. Thus, for instance, the continuous dropping of induced oil may be resolved by means of a separate reservoir, while advantage should by all means be given to a central lubrication system, if possible. In the machines with individual fills, the service life of conventional emulsion is around five weeks. In central lubrication systems, the same emulsion may last approximately twice longer, and without special care or maintenance. Emulsions's service life may be extended by building the necessary parts into the working machinery, such as centrifuges for the separation of induced oil, magnetic separators, and filter-bands for removing metal particles, grinding material, and other. If the evaporated water is made up for by demineralized water, it doubles once again, now totalling around 40 work weeks. Figure 2 shows how the extension of emulsion service life cuts down expenses - in this case implying material and waste management expenses.

Working emulsions prepared out of water-miscible metalworking fluid concentrates most frequently have a 2-10% concentration. The concentration depends on the given application requirements. Working emulsions are prepared at the plants just before their application, by mechanical pouring of the concentrate into the water. Emulsions may also be prepared using the so called injectors, in which case attention must be paid not to be "in the neutral", which could cause air bagging in into water, thus disturbing the emulsion's compositional balance. Water should be as pure as possible in the bacteriological sense, neutral, and have a specific hardness. The best one to use is drinking water, while that coming from rivers or that technological is not recommended without prior purification. One must stress that drinking water is usually hard. Due to high calcium content, it may create concretion, while the evaporation occuring at application causes the salt content to increase, thus reducing the fluid's service life. That is why some of the water softening methods may be applied, such as the ones using ionic exchangers, chemical treatment, and the like.

During the application of water-miscible metalworking fluids, there are several factors impairing emulsion and solution stability, thus reducing their service life. They are: Exhaustion of active substances, presence of impurities, influx of induced oil, cleaning agents, and salt, attack of microorganisms, water evaporation, penetration of different water hardnesses, and the like. Active substances, and especially emulsifiers, may be exhausted by their very use up for operation, as well as by the activity of microorganisms, and through oxidation. The presence of impurities: For instance metal or graphite particles during the working of cast iron, make the system unstable with their high adsorption due to their large specific surface, while they also serve as microorganism carriers. Induced oil, coming usually from the slideways and the hydraulic parts, creates a film on the emulsion surface preventing it from coming into contact with air and thus providing the anaerobic bacteria with conditions for emulsion disintegration and unpleasant odour appearance, the so called monday morning smell, resulting from microbiological disintegration. The induced oil film may also serve as a microorganism - especially mould - carrier, which is why the oil must regularly be removed from the surface. It is necessary to ensure emulsion stirring during machine standstill due to its ventilating, as well as a constant emulsion refreshment during application. During fill exchanges, the working emulsion is frequently contaminated by cleaning agents. Waters for making working emulsions are usually hard, containing different anions and cations. The entrance of electrolytes weakens emulsifier efficiency when creating an oriented emulsion system i.e. reduces emulsion stability. The power of electrolyte impact lies in the following sequence: Anions SO_4^{2-} > CH_3CO^{2-} > Cl^- > Br^- > NO_3^- > ClO_3^-, and cations Mg^{2+} > Ca^{2+} > Sr^{2+} > Ba^{2+} > Li^+ > Na^+ > K^+, etc. During long-term operation, the salt concentration increases due to evaporation. According to the sequence of power of individual ions, it is obvious that their salts behave similarly. And so, the sequence of salts with the most impact on emulsion stability is as follows: $MgSO_4$ > Na_2SO_4 > $(NH_4)_2SO_4$. It is very little known that water hardness has a major impact on microorganism growth in working emulsions. The most active salts from water are calcium and magnesium chloride, and calcium and magnesium carbonate in concentrations of up to 1,500 ppm. Above that value, they act as inhibitors. The basic working fluid applicative properties that must be evaluated daily are as follows: Solution level, odour, appearance - penetration of oil, impurities, corrosion instances on the machine, but also on workpieces; sticking, and foaming. Regular analytical analyses for emulsion monitoring are also of major significance (13). It is useful to make an analyses plan of the kind used, for instance, at a large German automobile factory (Table 2).

THE EXPERIMENTAL PART

The Purpose of Testing

The paper has tried to perform a practical examination of the biostable cooling and lubrication fluid performances in different metalworking operations and at different plants. We have been following four systems with defined concentration working emulsions. The objectives were different and dependent on the requirements set by either the system itself or the consumer, from meeting the worked surface quality, good washing out, corrosion protection, to resistivity towards microbiological contamination. Table 3 shows the test emulsions' working machinery and operating conditions, types of metal worked, as well as the given exploitation time.

Test Fluid

The test fluid is a semi-synthetic biostable emulsifying metalworking fluid blended in keeping with the latest human health and environmental protection requirements in the area of metalworking. Total aromatic content has been reduced, so that low aromatic content paraffin-based mineral oil was used. Instead of alkylbenzene derivatives - so far the most spread emulsifier group

- we have used a blend of natural acids and fatty acid derivatives. Boric acid derivative was used as corrosion inhibitor and microorganism growth regulator. This formulation does not contain compounds of chlorine, diethanolamine (DEA), nitrites, nitrates, or any other "negative list" compounds. Concentrate and emulsion properties are shown in Table 4.

TEST RESULTS AND DISCUSSION

The new biostable emulsifying metalworking fluid was tested on several metalworking machines at several plants. Emulsions to be tested on individual machines were prepared according to the plants' possibilities, mostly by pouring the concentrate into the water. Table 5 shows test results of working emulsion samples on the universal grinder UFD 1000 Kikinda. The test began towards the end of summer and lasted for four months. The emulsion's working hours lasted through two shifts, while standstills occured on weekends, for 2 days, and on holidays, 5-10 days. The samples were initially taken every week, and later on twice a month. A 2% concentration was used for the grinding operation. The results show that the concentration ranges from 1.8-2.6%, while it is dependent on the handling of the workpieces, evaporation, and topping up. Alkali reserves drop during application. Since the methods of concentration determination do not match, we may conclude that induced oil penetrates the emulsion, obstructing the measurement of concentration using a refractometer by increasing the value. Corrosion determination reveals that corrosion protection properties decrease, which could be caused by the lowered concentration of the cooling and lubricating fluid itself, induced oil penetration, salt concentration increase due to evaporation, and partially also microorganism activity. The number of microorganisms was low at application, but it increased towards the end, caused by a high induced oil concentration, as well as by that of fine metal and grinding material particles i.e. lower real emulsion concentration. Out of the usual microorganism types, we have isolated only the aerobic mesophylic bacteria indicating total bacteria number, and moulds. The freshening up of the working emulsion improved the condition and the work was continued (for over a year). According to employee reports, there was no corrosion, sticking, unpleasant odour, or skin or respiratory organs reactions near the machine.

Table 6 shows the results of testing working emulsion samples from the universal semi-automatic milling machine NC Norte HS1. A 5% concentration has been set and subsequently blended, since various types of metals - from non-ferrous ones to tool steel - are being worked on this machine through various kinds of operations. The analysis results reveal pH-value stability ranging from 8.8-9.13. Corrosion protection checked through Herbert and filtre paper tests has been constant throughout the period. Foaming was greater at the beginning, due to relatively low water hardness, while it decreased in time. The number of microorganisms was slowly increasing during application, but did no go over 10^4.

During operation, oil from the sliding tracks penetrated into the emulsion, increasing concentration at refractometer measurement. This may be seen from laboratory analyses as well. By comparing concentrations calculated using the following three methods: Through oil content determination by acid splitting; alkali reserves, and refractometer, it may be observed that the concentrations do not match, Figure 3. Alkali reserves show the real concentration the best. On two occasions, the concentration determined by acid splitting was lower than that determined by refractometer, on the 37th and 39th workday respectively, resulting from i.e. indicating oil removal from emulsion surface using the industrial vacuum pump.

E3 emulsion is applied In the Honsberg central emulsion supply system for the treatment of engine casing made of cast iron. The total of 16 machines is connected by the lubrication system, involving different stages of casing production - from side milling, grinding, drilling, deep drilling, inclined drilling, to honing. The generated particles are washed off with the emulsion and taken to the emulsion reservoir containing 11,000 litres of emulsion. Metal particles are being continuously extracted here using a mechanical transporter, with the isolation of finer particles using cyclones. The emulsion is stirred continuously and driven through the channels. The reservoir also provides emulsion airing. The system is burdened by induced oil penetration at instances of pipe breakage, but also from the sliding paths, which is why an oil separator should be installed, thus prolonging the emulsion's service life. For the time being, oil is being collected using pumps. Individual machine operators use gloves, primarily due to large and sharp chips, thus improving emulsion care and employee hygiene. The results of testing the E3 test emulsion at application in the central system are shown in Table 7. The set testing time was three months. The results show that there has been a constant concentration increase during measurements using refractometer, and also with acid splitting, while alkali reserves remained the same. The lack of concentration match using different methods points to the presence of a pollutant, - in this case, the induced oil. The cause of oil penetration is a more pronounced hydraulic oil leakage from one of the machines. Since all of the emulsion - through channels and pipes - ends up at the joint reservoir, the oil contaminates the entire emulsion volumes. pH-value was mostly constant, with a single exception: On the 95th workday, when it dropped. The reason for the pH-value decrease lies in increased microbiological activity. Deposits have been observed in pipelines and filtres on the edge of the container. Microbiological analysis has established that the deposits were generated through the activity of mould called Acremonia; there were 1,500 of them in 1ml (14). The development of these mould - whose spores are highly resistant and may survive rather long in highly unfavourable conditions - was encouraged by high summer temperature, standstill during the summer vacation, low bacterial number, and even the additional food present due to the induced oil influx. There was no chemical intervention on that particular occasion, only the mechanical cleaning of deposits. After cleaning, the emulsion resumed its usual operation.

Table 8 shows laboratory test results of working emulsion E4 samples on a semi-automatic milling machine TOS MFA 6. Through milling operation, the lifter platform cogs were installed through the milling operation. The platform has 28 teeth, the module has 7, while their depth is 15.3 mm. The rotating table rotates on 63 revolutions per minute, and the tool on 84, with a distortion of 0.96 mm per minute. Tool grinding was been envisaged at the grinding machine, after 18 workpieces treated, whereas during the application of this particular emulsion, the period between two consecutive grindings has been extended. The operation of the machine in the production process proceeds in three shifts. Oil from the drive reductor constantly penetrates the working emulsion, requiring a more frequent floating oil removal.

Microbiological analysis has tested the working emulsions resistance to microorganism development from the surroundings. Nine microorganism types were determined, as shown in Table 9. Only two kinds were isolated out of everything else: Mould and aerobic mesophyllic bacteria, indicating total bacterial number. The number of microorganisms in E4 emulsion samples is much lower than 10^4, which is considered to be a normal population in biostable fluids. It should be pointed out that, in the emulsion from the former MFA 6 milling machine fill (by a different manufacturer), we have isolated Pseudomonas aeruginosa: 100,000 colonies in a millilitre. The emulsion had an unpleasant odour caused by the very aforementioned bacteria, which, apart from that, also has a negative impact on human eyes and skin (emulsion sample of 19 August).

At the end of the set emulsion working period, we have determined the total number of microorganisms ranging around the value of 10^4, which is considered satisfactory for biostable emulsions (Table 10). It may be observed that mould and fungi are present in all four working emulsions, while special bacteria were not isolated in any of them. In the E3 emulsion, a special mould type was isolated precisely after the set time of three months. Owing to the mechanical cleaning of deposits and fresh emulsion addition, there was no further growth. We may conclude that the new emulsifying fluid holds the total number of bacteria rather low, while the pathogenic species that do enter the emulsion soon stagnate in growth and eventually die.

Corrosion properties of working emulsions have remained pretty good even after rather long operation, as seen in Table 11. This particular emulsion has been formulated primarily for the working of iron materials. Herbert and filtre paper methods have revealed its very good anti-corrosion protection even after a prolonged exploitation period. A good corrosion protection of non-ferrous metals requires concentration of over 2%, which is seen in emulsion E1, with the concentration of 1.8%. Emulsion E3 contains a very high quantity of induced oil, which is why it does not provide good brass protection.

Based on the results of working emulsions testing, as well as based on experience gained at various plants, we may say that biostable emulsion formulations have provided good properties of cooling, corrosion protection, resistance towards microorganisms, but also excellent lubrication properties. Due to their semi-transparent appearance, the working emulsions enabled better supervision of the working zone. At production plants, the emulsions generated no unpleasant odours; did not cause machines to be repaired or paint to come off. Emulsions did not cause allergy symptoms with workers, such as dermatological problems or difficulties with breathing. There was no need to add chemical agents such as antifoamers, bactericides, or fungicides. All the emulsions have continued their operation. Some have been in the machinery for over a year now.

Due to a constant leading away of a part of the emulsion with metal particles and workpieces, and due to the constant presence of water evaporation, fresh emulsion with either lower or higher concentration was being topped up, depending upon whether it was thickened or dissolved during the production process. Some plants have working emulsion corrections organized weekly, and some daily, depending on the already existing habits of those in charge of maintenance at plants or machine operators. In cases of too high oil penetration, Norte and MFA 6, the oil was, whenever necessary, removed using industrial vacuum pumps. This is a special formulation intended for the working of iron materials. Due to a carefully selected blend of corrosion inhibitors, it may be applied also for non-ferrous metals, which has been proven through various kinds of operations on the NORTE turning-lathe while working aluminum and other materials.

CONCLUSION

The concern for occupational safety and environmental protection has been growing increasingly important with regard to the existing technical requirements. Safety and environmental protection have a major impact on the development of feeds, on formulations, and also on metalworking fluid manufacturers. In the present paper, we have shown the applicative properties of the new metalworking fluid. It is a semi-synthetic emulsifying fluid, generating biostable emulsions with water. Its composition meets with modern requirements associated with occupational safety and environmental protection. The said biostable emulsion has met the required conditions in all working phases - from cooling, lubrication, and washing out, to being neutral for those handling it and having resistivity towards the growth of microorganisms. In all systems, it has met the said deadline of three months, and continued working for over a year without any problem.

The long service life of the biostable emulsion was supported also by maintenance undertaken in individual plants.

The application of the biostable emulsion has advanced industrial hygiene, reduced waste emulsion volumes, while also the overall costs were reduced, all of this contributing to Total Fluid Management.

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621.899 otpadno ulje	wasted oil

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