Tribološka svojstva deterdženata kao aditiva za motorna ulja

A.I. Dotsenko¹, V. D. Samusenko^{1*}

¹ Nacionalni Moskovski državni univerzitet za građevinarstvo

Sprovedena istraživanja u širokom temperaturnom opsegu anti-friktionih karakteristika deterdženta - fenolata i kalcijum sulfonata različitih nivoa alkalnosti kao aditiva u polialfalolefinskom ulju. Utvrđeno je da glavna uloga u formiranju graničnih slojeva podmazivanja deterdženta pripada kalcijum karbonatu.

Ključne reči: deterdženti; ulje za podmazivanje; dvotaktni benzinski motori; temperatura; koeficijenti trenja

1. UVOD

Deterdžent - to je površinski aktivna supstanca. Sadrži molekule koji su u stanju da drže okrugle čestice masti i ispere ih sa površine.

Uticaj površinski aktivnih materija kao deterdženta se trenutno ispituje adekvatno. Istovremeno, pitanja vezana za proučavanje triboloških osobina deterdženata, kao aditiva za motorna ulja, još nisu dovoljno proučavana i predmet su istraživanja na Nacionalnom Moskovskom državnom univerzitetu za građevinarstvo [1].

Istraživanje triboloških osobina deterdženata realizovano je za dvotaktne benzinske motore.

Dvotaktni benzinski motori se uglavnom koriste tamo gde su kritični parametri izbora velike snage, lagane konstrukcije i niske cene (na primer, bespilotne letve, skuteri, motorne testere, građevinska oprema, vanbrodske aplikacije itd.). Jedna od glavnih karakteristika rada dvotaktnih motora je odsustvo sistema za podmazivanje u njima. Ulje ne cirkuliše, a preporučena količina motornog ulja razblažuje se u gorivu, a kroz karburator ta mešavina goriva i ulja stiže do motora. Smeša prolazi kroz motor velikom brzinom, deo ulja u obliku tankog filma se zasniva na detaljima i podmazuje. Ostatak ulja sagoreva zajedno sa gorivom u komori za sagorevanje. Jednostavni motori, koriste način mešanja koji se sastoji u tome što se odgovarajuća količina ulja meša ručno sa benzinom od 1:20 do 1:100.

U tom pogledu povećani su zahtevi za kvalitetu ulja za dvotaktne benzinske motore. Najvažnije su: sprečavanje intenzivnog habanja i prажnjenja; sprečavanje stvaranja depozita na detaljima u komori za sagorevanje [2]. Takođe, veliki značaj je dobio ekološki zahtev.

Tokom razvojnih ulja za dvotaktne benzinske motore, različita istraživačka oprema - pretvarač aparat za oscilovanje [3, 4], mašina za ispitivanje sa četiri loptice [5] primenjuje se na inicijalnu procenu svojstva maziva.

Kao važna karakteristika motornih ulja koja imaju značajan uticaj na podmazivanje svojine je njihova termička stabilnost pri trenju. U ovom radu korišćena je metoda temperature [5] za dobijanje karakteristika trenja temperature izabranih ulja. Tako je korištenjem ove metode u

četvorotaktnim motorima sa unutrašnjim sagorevanjem utvrđena inverzna korelacija između kritičnih temperatura nekoliko motornih ulja i habanja klipnih prstenova [6]. Preliminarna procena posledica analize rezultata triboloških ispitivanja ulja za dvotaktne benzinske motore ovim metodom omogućava procenu mazivnih svojstava ulja s širokim opsegom temperature i nivoom depozita po detalju.

2. PREDMET STUDIJE

Predmeti studije o podmazivanju svojstava deterdženata su kalcijum sulfonati, koji su jedan od najčešće korištenih deterdženata u trenutnim motornim uljima. Korišćeni sulfonati se razlikuju u vrednosti početnog baznog broja, koji se razlikuje u rasponu od 15–400 mg KOH/g (Tabela 1).

Da bi se isključio uticaj koloidne strukture deterdženata na njihovu tribološku karakteristiku, proučavani su u koncentraciji od 1.0 vol %, koji premašuje koncentraciju kritične micelne formacije proučavanih kompozicija. Aditivi su uvedeni u ulje poli alfa-olefina PAO-4 u gornjoj koncentraciji ($v_{100} \approx 4 \text{ mm}^2/\text{s}$). Ovo ulje ima visoku čistoću i izabrano je zbog minimalnog uticaja prirodnih deterdženata na ponašanje studiranih aditiva.

Poznato je da kalcijum sulfonat formira micelarni rastvor i da je koloidna disperzija kalcijum karbonata (CaCO_3) stabilizovana neutralnim sulfonatom [8]. Zauzvrat, disperzija CaCO_3 ima prosečnu veličinu čestica $<10 \text{ nm}$, gustinu od 2200 kg/m^3 (u poređenju sa $1200\text{--}1700 \text{ kg/m}^3$ u neutralnom sulfonatu) i karakteriše se kvazi-stabilnom (vateritom) obliku. U celini, 60-70% alkalnog rezerva aditiva određuje sadržaj CaCO_3 ; nakon povećanja koncentracije karbonata, bazni broj deterdženta se povećava (Slika 1).

Tabela 1. Osnovni brojevi proučavanih kalcijum sulfonata

Deterdžent	Osnovni broj, mg KOH/g
C1	15
C2	150
C3	175
C4	370
C5	400

* Kontakt adresa autora: Nacionalni Moskovski državni univerzitet za građevinarstvo, Moskva, 129337, Yaroslavl highway, 26

Sl. 1. Zavisnost baznog broja kalcijum sulfonata na sadržaj karbonata (CaCO_3). Grafikon je razvijen prema [9].

Prema strukturi i sastavu deterdženata, ne bi trebalo da pokazuju visoku reaktivnost prema metalima parnog frikcionog sistema sa formiranjem hemijski modifikovanih slojeva koji imaju značajan uticaj na procese trenja i habanja. Pod ovim uslovima, uticaj disperzije (CaCO_3) u sastav deterdženata, koji određuju njihovu alkalnost ili druge tehnološke dodatke, uglavnom je očigledan.

Deterdžent (kalcijum sulfonat) se može smatrati kombinacijom tri komponente, odnosno neutralnog kalcijum sulfonata, kalcijum karbonata (CaCO_3) i baznog ulja. Kao što je već rečeno, sadržaj kalcijum karbonata uglavnom određuje alkalnost aditiva: pod njegovim povećanjem, bazni broj se povećava. Neutralan kalcijum sulfonat uzrokuje malu dodatnu alkalnost aditiva zahvaljujući CaO i Ca(OH)_2 . Pretpostavlja se da iskorišćeno bazno ulje ne utiče na tribološke karakteristike ispitivanih deterdženata.

3. METODE

Testovi su izvedeni korišćenjem KT-2 (GOST 23-221) četvorostruka kočiona mašina [7], u kojoj je, kako bi se sprečilo primetno zagrevanje trenja, obezbeđena niska klizna brzina u sklopu trenja i uzorci trenja i okolni sloj ulja se zagreva pomoću spoljašnjeg izvora toplote. Uzorci su čelične kugle od 100Cr6 prečnika 7,94 mm. Aksijalno opterećenje je bilo 107.8 N, kontaktno opterećenje na jednoj lopti iznosilo je 44.2 N, a pritisak u kontaktu gornje i svake donje lopte (Hertz) bio je oko 2.1 GPa. Brzina klizanja na kontaktnoj površini iznosila je 0,24 mm/s (Slika 2).

Sl. 2: Mašina za trenje: 1 – termoelektrika; 2 – navrtka; 3 – tige; 4 – kuglica; 5 – ulje; 6 – okvir; 7 – čaša za ulje; 8 – zagrevanje; 9, 10 – oslonac

Studija je izvedena u temperaturnom opsegu od 30-300 °C, što je blizu temperatura ulja kod motora sa unutrašnjim sagorevanjem. Temperatura frikcionog sklopa povećana je stepenično pomoću spoljnog izvora toplote brzinom od 5 °C/min.

Koeficijent trenja je procenjen na svakih 10-20 °C. Dužina eksperimenta na svakoj temperaturi iznosila je 60 s. Procenjeni pokazatelji su zavisnosti koeficijenta trenja f na temperature T , tj. funkcija $f = F(T)$. Krive su razvijene korišćenjem prosečnih vrednosti tri testa.

Prednost ove tehnike u poređenju sa drugim metodama za procenu trenja i habanja leži u činjenici da promjena u f takođe pomaže u određivanju energije formiranja i uništavanja graničnih slojeva podmazivanja. Hemijski sastav površinskih slojeva kontaktnih tela određen je pomoću mikroskopa FEI Quanta 200 sa aparatom Apollo 40 za elementarnu analizu pomoću energetske disperzione spektroskopije [10].

4. REZULTATI I DISKUSIJA

Rezultati eksperimenata su prikazani na Slici 3. Iz dobijenih podataka proizilazi da dodavanje deterdženata u bazno ulje dovodi do značajnog smanjenja koeficijenta trenja u svim temperaturnim intervalima; Imajte na umu da, nakon povećanja osnovnog broja deterdženta, njegove tribološke karakteristike se poboljšavaju.

Sl. 3: Zavisnost koeficijenta trenja deterdženata sa različitim alkalitetima na temperaturi: (1) PAO-4; (2) PAO-4 + 1% C1; (3) PAO-4 + 1% C2; (4) PAO-4 + 1% C3; (5) PAO-4 + 1% C4; (6) PAO-4 + 1% C5. Šrafura označava zonu oštre promene koeficijenta trenja.

Krive zavisnosti koeficijenta trenja na temperaturi koja se razvija pod predviđenim uslovima su slične krivama dobijenim kao rezultat testiranja hemijski aktivnih aditiva [8]. Označiti prelazne temperature preko $Tt1$, $Tt2$, i $Tt3$.

Tabela 2. Rezultati ispitivanja ispitanih kompozicija maziva

Sastav maziva	T_{t1} , °C	T_{t2} , °C	T_{t3} , °C	f_{max}	f_{min}	Srednja d_w , μm
PAO-4	30	–	–	0.41	0.1315	234
PAO-4 + 1% C-1	70	210	250	0.1875	0.116	222
PAO-4 + 1% C-2	70	210	–	0.155	0.11	212
PAO-4 + 1% C-3	–	210	–	0.135	0.0935	206
PAO-4 + 1% C-4	–	160	260	0.0745	0.023	207
PAO-4 + 1% C-5	–	160	270	0.078	0.021	205

Pretpostavimo da je T_{t1} temperatura razaranja graničnog sloja, što je uzrokovano oštrim povećanjem koeficijenta trenja; T_{t2} je temperatura pri kojoj je modifikovan sloj formiran od površine trenja koji se manifestuje u smanjenju koeficijenta trenja koji ga postavlja na konstantnom nivou u određenom temperaturnom opsegu; T_{t3} je temperatura uništenja modifikovanog sloja, koja se manifestuje velikim porastom koeficijenta trenja. Vrednosti prelaznih temperatura i koeficijenti trenja na tipičnim temperaturama prikazani su u Tabeli 2

U slučaju PAO-4, smanjenje koeficijenta trenja na temperaturama prelazi T_{t1} očigledno uzrokuje činjenica da se u temperaturnom opsegu od 50-160 °C javlja intenzivna oštra promena koeficijenta trenja. Nakon završetka ovog perioda sledi stabilizacija koeficijenta trenja, što je verovatno prouzrokovano razbijanjem površina.

Sl. 4. Zavisnost koeficijenta trenja na baznom broju kalcijum sulfonata. (1) stabilna; (2) maksimalno

Za niski alkalni kalcijum sulfonat C1 i srednji alkalni C2, prisustvo intermedijarne temperature T_{t1} , što ukazuje na uništenje graničnog sloja adsorpcije, je tipično. U slučaju deterdženta C3 primećuje se neznatno povećanje koeficijenta trenja, što ukazuje na delimično uništenje graničnog sloja. Prilikom testiranja visoko alkalnih kalcijum sulfonata, koeficijent trenja je u početku manji i T_{t1} nije registrovana.

Osim toga, u određenom temperaturnom opsegu stabilizacija koeficijenta trenja na određenom nivou je tipična za ispitivane deterdžente, tj., intermedijarna temperatura T_{t2} , što ukazuje na formiranje modifikovanog sloja na površini trenja. Po povećanju alkalnosti, temperaturni opseg u kojem su slojevi slojeva stabilni takođe se povećava.

U slučaju visoko alkalnih deterdženata C4 i C5, na T_{t3} , uništavanje modifikovanih slojeva se javlja na 300 °C, a koeficijent trenja ostaje niži od koeficijenta trenja srednjih alkalnih kalcijum sulfonata C2 i C3. Za srednje alkalne kalcijum sulfonate C2 i C3, temperatura prelaska T_{t3} nije registrovana u posmatranom temperaturnom opsegu.

Na Slici 4 prikazane su zavisnosti koeficijenta trenja na maksimumu i stabilnosti (pretpostavljeni jednako 220 °C za sve kalcijum sulfonate) baznog broja deterdženta. Može se videti da se, nakon povećanja alkalnosti, vrednosti koeficijenta trenja smanjuju skoro linearno.

Uzorci pet komercijalnih ulja koje se primenjuju za podmazivanje dvotaktnih benzinskih motora su takođe testirani. Osnovne karakteristike ovih ulja prikazane su u Tabeli 3. Ulja C, D i E jednog proizvođača. Ulja D i E, prema kategorijama JASO i ISO, su ulja sa niskim dimom, a ulje E mora imati povećan efekat deterdženta. Prema klasifikacijama ISO, JASO i NMMA razlike u podmazivanju između ulja C, D i E nisu utvrđene. U klasifikaciji API-a nije prisutno posebno odvajanje sa podmazivanjem ulja, pored toga samo deluje kategorija TC.

Tabela 3. Osnovne karakteristike ulja

Ulje	Kinematički viskozitet pri 100 °C	Bazne rezerve	Ispunjavanje specifikacije
A	11,8	Mineralna	–
B	12	Mineralna	API TB
C	9,7	Mineralna	API TB, ISO-L-EGB, JASO FB, NMMA TC-W3
D	9,5	Polusintetička	API TC, ISO-L-EGC, JASO FC, NMMA TC-W3
E	8	Sintetička	API TD, ISO-L-EGD, JASO FD, NMMA TC-W3

Zbog detaljnih informacija o sastavu testiranih komercijalnih ulja za dvotaktne benzinske motore koje nam nisu dostupne, teško je precizno definisati šta utiče na termičku stabilnost ulja na određenoj temperaturi: struktura pakovanja aditiva ili baze ulja.

Među ispitivanim mineralnim uljima (Slika 5) najbolju toplotnu stabilnost je pokazalo ulje C. Za ovo ulje u ispitivanom opsegu temperatura kritična temperatura na kojoj se granični slojevi raspadaju nije otkrivena. Koeficijent trenja je stabilan i čini oko 0,1-0,12.

Ulja A i B imaju približno identičnu termičku stabilnost, a njihove kritične temperature su ~240 i ~230 °C respektivno. Ulje A pokazuje jednaku ili čak najbolju sposobnost podmazivanja. Na osnovu onoga što je moguće pretpostaviti da su korišćeni slični aditivi u kompoziciji pakovanja.

Sl. 5: Temperaturno-friktione karakteristike mineralnog ulja: 1 - ulje A, 2 - ulje B, 3 - ulje C.

Među uporednim uljima jednog proizvođača (slika 7), termička stabilnost mineralnog ulja C je najviša. Polusintetičko ulje D ima srednju poziciju.

Sl. 6: Fotografije čepova nakon ispitivanja ulja: a - ulje C; b - ulje D; c - ulje E.

Sl. 7: Temperaturno-friktione karakteristike ulja jednog proizvođača: 1 - ulje C, 2 - ulje D, 3 - ulje E.

Sintetičko ulje E u ispitivanom opsegu temperatura pokazalo je najgoru moć podmazivanja gotovo u svim intervalima proučavanih temperatura.

Nekoliko vrhova na grafiku temperaturnog trenja karakterističnog za ulje E pokazuju da njegova formulacija sadrži ne manje od dva hemijski aktivna dodatka koji formiraju hemijski modifikovane slojeve koji omogućavaju smanjenje koeficijenta trenja u različitim rasponima temperatura na površinama trenja[8]. Uništavanje modifikovanih slojeva koji odvajaju površinu za trljanje reflektuju se u oštrom povećanju koeficijenta trenja nakon 250 °C. Niska sposobnost podmazivanja ulja E (sintetičko) u poređenju sa uljima C (mineralno) i D (polusintetičko), očigledno, objašnjava se činjenicom da je sintetičko ulje koje je bazna materija praktično ne oksidira pri porastu temperature u proučavanom intervalu dok ulja na mineralnoj (pa čak i na polusintetičkoj osnovi) oksidiraju, što povećava sposobnost podmazivanja proučavanih maziva. Pogoršanje sposobnosti podmazivanja može biti povezano i sa činjenicom da proizvođač koristi manju količinu aditiva za smanjenje dima i količinu depozita u komori za sagorevanje. Na Slici 6. Prikazane su fotografije čepova shows the photographs of mandrels nakon ispitivanja ulja jednog proizvođača. Razlika između čepova je vizuelno dobro prepoznatljiva. Dakle, čep nakon ispitivanja mineralnog ulja C ima najveće zatamnjenje, a u slučaju sintetičkog ulja E tragovi uticaja visokih temperatura su minimalni. Na taj način je moguće razvrstati ulja na detergentnosti $C < D < E$. Dobijeni podaci odgovaraju karakteristikama ulja njihove detergentije deklariranih u klasifikacijama JASO i ISO.

5. ZAKLJUČAK

Stoga, proučavanje tribološke karakteristike deterdženata za motorna ulja u slučaju kalcijum sulfonata različitih alkaliteta utvrdilo je pozitivnu ulogu kalcijum karbonata u sastavu micelijuma aditiva. Ovo ne samo da obezbeđuje neophodnu alkalnost aditiva, već i utiče na smanjenje koeficijenta trenja.

Na osnovu hemijske analize površine uzorka, može se pretpostaviti da, pored povećanja temperature, potrebno je i trenje za formiranje zaštitne folije na površini.

Izvedena studija pokazuje da je uticaj aditiva za deterdžent (bar, kalcijum sulfonat) na maziva svojstva ulja veoma značajan i treba ga uzeti u obzir prilikom izrade mazivnih sastojaka.

Utvrđena je mogućnost diferenciranja ulja za dvotaktne benzinske motore na osnovu sposobnosti podmazivanja, a takođe i detergentije pomoću temperaturnog metoda procene sposobnosti ulja za podmazivanje.

U postavljenim uslovima najbolju termičku stabilnost pokazalo je ulje C na mineralnoj osnovi. Ulja na mineralnoj osnovi A i B su pokazala blisku termičku stabilnost koja predlaže slične pakete aditiva. Ulje E na sintetičkoj osnovi pokazalo je

najveći koeficijent trenja skoro pri svim temperaturama.

Vizuelna procena čepova nakon testiranja omogućava procenu detergencije ulja. Najmanje od svih tragova uticaja na temperaturu je pri upotrebi sintetičkog ulja E koji će biti usklađeno sa klasifikacijama JASO i ISO.

LITERATURA

- [1] Dotsenko A.I., Buyanovskij I.A. Osnovy tribotekhniki. M: Infra-M, 2014. 335 s.
- [2] Meshcherin E.M., Ostrovskaya M.E. Oils for two-stroke petrol engines. Thematic review. – M.: TSNIITEHneftekhim, 1989. – 72 pp.
- [3] Igartua A., et al. Alternative eco-friendly lubes for clean two-stroke engines. Tribology International 44.6 (2011): 727–736.
- [4] Singh A. K. Castor oil-based lubricant reduces smoke emission in two-stroke engines. Industrial crops and products 33.2 (2011): 287–295.
- [5] Kumar G. S., Balamurugan A., et al. Tribological and emission studies on two stroke petrol engine lubricated with sunflower methyl ester. J Sci Ind Res 71 (2012): 562–565.
- [6] Matveevsky R.M., Lashkhi V.L., Buyanovsky I.A. et al. Lubricants. Antifrictional and antiwear properties. Test methods. – M.: Mashinostroenie, 1989. 192 pp.
- [7] ZHilko V.N., Buyanovsky I.A., Lisenkov Yu.G. About bond between temperature firmness of engine oils and their antiwear properties. Friction and wear T.4, № 4 (1983): 724–727.
- [8] Matveevsky R.M., Buyanovsky I.A., Karaulow A.K., et al. Transition temperatures and tribochemistry of the surfaces under boundary lubrication. Wear 136.1 (1990): 135–139.
- [9] Glavati O.L. Fiziko-khimiya dispergiruyushchikh prisadok k maslam. Kiev: Naukova Dumka, 1989.
- [10] Stachowiak G., Batchelor A.W. Experimental Methods in Tribology. Amsterdam, 2004

Tribological Properties of Detergents as Additives for Motor Oils

A.I. Dotsenko, V. D. Samusenko^{1*}

¹ National Research Moscow State University of civil engineering

Conducted research in a wide temperature range anti-friction properties of detergent – phenolate and calcium sulfonates of different levels of alkalinity as additives to polyalphaolefine oil. It is found that in the formation of a detergent of boundary lubricating layers main role belongs to the calcium carbonate.

Keywords: detergents, lubrication oil; two-stroke petrol engines; temperature; coefficients of friction

0. INTRODUCTION

Detergent – it is a surface-active substance. It contains molecules that are able to stick round grease particles and rinse them from the surface.

The influence of surfactants as detergents is currently studied adequately. At the same time, the issues associated with the study of the tribological properties of the detergents, as additives for motor oils, is not yet sufficiently studied and are the subject of research in National Research Moscow State University of civil engineering [1]. Study of tribological properties of detergents was realized for two-stroke petrol engines.

Two-stroke petrol engines are used mainly where critical parameters of the choice are the high power density, lightweight and low price (for example, drones, scooters, chainsaws, construction equipment, outboard applications, etc). One of the main features of operation of two-stroke engines is absence of the lubrication system in them. Almost in all two-stroke engines the total-loss lubrication is applied. Oil does not circulate, and the recommended amount of motor oil is diluted in fuel, and through the carburetor this fuel and oil mixture gets to the engine. Mixture passes through the engine with a high speed, the part of oil in the form of a thin film settles on details, and it lubricate. The rest of oil burns down together with fuel in a combustion chamber. Simple engines, use the way of mixing which is that the corresponding oil quantity mixes up manually with petrol concerning from 1:20 to 1:100.

In this regard increased requirements are imposed to quality of oils for two-stroke petrol engines. Are the most important: prevention of intensive wear and scuffing; prevention of formation of deposits on details in a combustion chamber [2]. Also big importance was gained by ecological requirements.

During development oils for two-stroke petrol engines the different research equipment – translator oscillation apparatus [3, 4], four-ball test machine [5] is applied to an initial assessment of lubricant property.

As the important characteristic of motor oils exerting considerable impact on lubricating property is their thermal stability at friction. In this work, were used a temperature method [5] for receiving temperature–friction characteristics of the chosen oils. So using this method

the inverse correlation between critical temperatures of a number of motor oils and wear of piston rings has been established in four-stroke internal combustion engines [6]. The preliminary estimate in consequence of the analysis of results the tribological tests of oils for two-stroke petrol engines by this method allows to evaluate lubricating properties of oils with the broad range of temperatures and the level of deposits on details.

1. THE OBJECT OF THE STUDY

The objects of a study of the lubricating properties of detergents were calcium sulfonates, which are one of the most widely used detergents in current motor oils. The used sulfonates differ in the value of the initial base number, which varied in the range of 15–400 mg KOH/g (Table 1).

To exclude the influence of the colloidal structure of detergents on their tribological characteristic, they were studied at a concentration of 1.0 vol %, which exceeds the concentration critical micelle formation of the studied compositions. The additives were introduced in poly alpha olefin oil PAO-4 in the above concentration ($v_{100} \approx 4$ mm²/s). This oil has a high purity and was chosen due to the minimum influence of natural detergents on the behavior of the studied additives.

It is known that calcium sulfonate forms a micellar solution and is a colloidal dispersion of calcium carbonate (CaCO₃) stabilized by neutral sulfonate [8]. In turn, the CaCO₃ dispersion has an average particle size of <10 nm, a density of ~2200 kg/m³ (versus 1200–1700 kg/m³ in neutral sulfonate), and is characterized by a quasi-stable form. On the whole, 60–70% of the alkali reserve of the additive is determined by the CaCO₃ content; upon an

Table 1. Base numbers of the studied calcium sulfonates

Detergent	Base number, mg KOH/g
C1	15
C2	150
C3	175
C4	370
C5	400

Fig. 1. Dependence of the base number of calcium sulfonates on the content of carbonates (CaCO_3). Graph is developed according to [9].

increase in the carbonate concentration, the base number of the detergent increases (Fig. 1).

According to the structure and composition of detergents, they are not supposed to demonstrate high reactivity toward metals of a friction pair with the formation of chemically modified layers that have a noticeable influence on the friction and wear processes. Under these conditions, the influence of dispersions (CaCO_3) in the composition of detergents, which determine their alkalinity, or other technological admixtures is mainly apparent.

The detergent (calcium sulfonate) can be considered to be a combination of three components, namely, neutral calcium sulfonate, calcium carbonate (CaCO_3), and base oil. As mentioned above, the content of calcium carbonate mainly determines the alkalinity of the additive: under its increase, the base number increases. Neutral calcium sulfonate causes a slight additional alkalinity of the additive owing to CaO and Ca(OH)_2 . It is assumed that the used base oil does not noticeably influence the tribological characteristics of the studied detergents.

2. METHODS

The tests were performed using a KT-2 (GOST 23-221) four-ball friction machine [7], in which, in order to prevent noticeable friction heating, low sliding speed in the friction assembly is provided, and friction samples and the surrounding oil layer are heated using an external heat source. Samples were 100Cr6 steel balls with a diameter of 7.94 mm. The axial load was 107.8 N, the contact load on one ball was 44.2 N, and the pressure in the contact of the upper and each of the lower balls (Hertz) was about 2.1 GPa. The sliding speed on the contact surface was 0.24 mm/s (Fig. 2).

The study was performed in the temperature range of 30–300°C, which is close to the oil temperatures in internal combustion engines. The temperature of the friction assembly increased stepwise using an external heat source at a rate of 5°C/min. The coefficient of friction was evaluated every 10–20°C. The duration of the experiment at each temperature was 60 s. The estimated indicators were the dependences of the coefficient of friction f on the temperature T , i.e., the function $f = F(T)$. The

Fig. 2. The machine of friction: 1 – thermoelectrifier; 2 – nut; 3 – tige; 4 – ball; 5 – oil; 6 – mounting; 7 – beaker for oil; 8 – worming up; 9, 10 – support

curves were developed using the average values of three tests.

The preference of this technique compared to other methods for evaluating the friction and wear lies in the fact that the change in f also helps to determine the energy of the formation and destruction of the boundary lubricating layers. The chemical composition of the surface layers contacting bodies was determined using a FEI Quanta 200 scanning microscope with an Apollo 40 device for elemental analysis by energy dispersive spectroscopy [10].

3. RESULTS AND DISCUSSION

The results of the experiments are shown in Fig. 3. It follows from the obtained data that the addition of detergents in base oil leads to a significant decrease in the coefficient of friction in all the temperature interval; note that, upon a increase in the base number of the detergent, its tribological characteristics improve.

Fig. 3. Dependence of coefficient of friction of detergents with different alkalinities on the temperature: (1) PAO-4; (2) PAO-4 + 1% C1; (3) PAO-4 + 1% C2; (4) PAO-4 + 1% C3; (5) PAO-4 + 1% C4; (6) PAO-4 + 1% C5. Hatching denotes the zone of the sharp change in the coefficient of friction.

Table 2. Testing results of the studied lubricant compositions

Lubricant composition	T_{t1} , °C	T_{t2} , °C	T_{t3} , °C	f_{max}	f_{min}	Average d_w , μm
PAO-4	30	–	–	0.41	0.1315	234
PAO-4 + 1% C-1	70	210	250	0.1875	0.116	222
PAO-4 + 1% C-2	70	210	–	0.155	0.11	212
PAO-4 + 1% C-3	–	210	–	0.135	0.0935	206
PAO-4 + 1% C-4	–	160	260	0.0745	0.023	207
PAO-4 + 1% C-5	–	160	270	0.078	0.021	205

The curves of the dependence of the coefficient of friction on the temperature developed under preset conditions are similar to the curves obtained as a result of testing chemically active additives [8]. Denote the transitional temperatures through T_{t1} , T_{t2} , and T_{t3} . Assume that T_{t1} is the boundary layer destruction temperature, which is caused by the sharp increase in the coefficient of friction; T_{t2} is the temperature at which a modified layer is formed of the friction surface, which manifests in a decrease in the coefficient of friction establishing it at a constant level in a certain temperature range; T_{t3} is the destruction temperature of the modified layer, which manifests in a sharp increase in the coefficient of friction. The values of the transitional temperatures and the coefficients of friction at typical temperatures are shown in Table 2.

In the case of PAO-4, the decrease in the coefficient of friction at temperatures exceeding T_{t1} is apparently caused by the fact that, in the temperature range of 50–160°C, the intense sharp change in the coefficient of friction occurs. After the completion of this period, the stabilization of the coefficient of friction follows, which is probably caused by the breaking-in of surfaces.

Fig. 4. Dependence of the coefficient of friction on the base number of calcium sulfonate. (1) stable; (2) maximum

For low alkaline calcium sulfonate C1 and middle alkaline C2, the presence of the intermediate temperature T_{t1} , which indicates the destruction of the adsorption boundary layer, is typical. In the case of detergent C3, an insignificant increase in the coefficient of friction is observed, which indicates the partial destruction of the boundary layer. When testing highly alkaline calcium sulfonates, the coefficient of friction is initially lower and T_{t1} is not registered.

In addition, in a certain temperature range, the stabilization of the coefficient of friction at a certain level is typical for the studied detergents, i.e., the intermediate temperature T_{t2} , which indicates the formation of a modified layer on the friction surface. Upon an increase in alkalinity, the temperature range in which the boundary layers are stable also increases.

In the case of highly alkaline detergents C4 and C5, at T_{t3} , the destruction of the modified layers occurs at 300°C, and the coefficient of friction remains lower than the coefficients of friction of middle alkaline calcium sulfonates C2 and C3. For middle alkaline calcium sulfonates C2 and C3, the transition temperature T_{t3} is not registered in the studied temperature range.

In Fig. 4, the dependences of the coefficients of friction on the maximum and the stable (assumed equal to 220°C for all calcium sulfonates) base number of the detergent are shown. It can be seen that, upon an increase in alkalinity, the values of the coefficients of friction decrease almost linearly.

Samples of five commercial oils applied to lubricant of two-stroke petrol engines were tested also. The basic characteristics of these oils are shown in Table 3. Oils C, D and E of one manufacturer. Oils D and E, according to the categories JASO and ISO, are low-smoke oils, and oil E has to have the increased detergent effect. According to classifications of ISO, JASO and NMMA of distinction in lubricating ability between oils C, D and E are not established. In classification of API the distinct separation by lubricating ability of oils is not present, besides only the category TC is acting.

Table 3. The basic characteristics of oils

Oil	Kinematic viscosity at 100 °C	Base stocks	Meeting the specification
A	11,8	Mineral	–
B	12	Mineral	API TB
C	9,7	Mineral	API TB, ISO-L-EGB, JASO FB, NMMA TC-W3
D	9,5	Semisynthetic	API TC, ISO-L-EGC, JASO FC, NMMA TC-W3
E	8	Synthetic	API TD, ISO-L-EGD, JASO FD, NMMA TC-W3

Because of detailed information about composition of the tested commercial oils for two-stroke petrol engines is

not available to us, it is difficult to define precisely what influences on the thermal stability of oils at a certain temperature: structure of a package of additives or base oil.

Among the tested mineral oils (Fig. 5) the best thermal stability was shown by oil C. For this oil in the studied range of temperatures the critical temperature at which boundary layers collapse is not revealed. The friction coefficient is stable and makes about 0,1-0,12.

Oils A and B have approximately identical thermal stability, and their critical temperatures ~ 240 and ~ 230 °C respectively. Oil A shows equal or even the best lubricating ability. On the basis of what it is possible to assume that similar in composition packages of additives were used.

Fig. 5. Temperature-friction characteristics of mineral oil: 1 – oil A, 2 – oil B, 3 – oil C.

Among the compared oils of one manufacturer (fig. 7) thermal stability of mineral oil C the highest. Semisynthetic oil D takes an intermediate position.

Fig. 6. Photographs of a mandrel after testing of oils: a – oil C; b – oil D; c – oil E.

Fig. 7. Temperature-friction characteristics of oil from one manufacturer: 1 – oil C, 2 – oil D, 3 – oil E.

Synthetic oil E in the studied range of temperatures has shown the worst lubricating ability almost in all interval of the studied temperatures. Several peaks on graphics of temperature-friction characteristic of oil E demonstrate that its formulation contains not less than two chemically active additives forming chemically modified layers providing decrease in friction coefficient in the different ranges of temperatures on friction surfaces [8]. Destruction of the modified layers separating the rubbing surfaces is reflected in sharp raising of friction coefficient after 250 °C. Low lubricating ability of oil E (synthetic) in comparison with oils C (mineral) and D (semisynthetic), apparently, is explained by the fact that the synthetic oil which is an base stock is practically not oxidized at temperature increase in the studied interval while oils on mineral (and even on semisynthetic basis) are oxidized that increases lubricating ability of the studied lubricants. Deterioration in lubricating ability can be also connected with the fact that the manufacturer uses a smaller quantity of additives to reduce smoke and the amount of deposits in a combustion chamber. In fig. 6 shows the photographs of mandrels after tests of oils of one manufacturer. The difference between mandrels is visually well distinguishable. So the mandrel after testing of oil of mineral oil C has the greatest darkening, and in a case with synthetic oil E traces of influence of high temperatures are minimum. It is possible to range oils on their detergency thus C<D<E. The obtained data correspond to the characteristics of oils of their detergency declared in classifications of JASO and ISO.

4. CONCLUSION

Hence, the study of the tribological characteristic of detergents for motor oils in the case of calcium sulfonates of different alkalinities established the positive role of calcium carbonate in the composition of a micelle of the additive. This not only provides the required alkalinity of the additive, but also influences a decrease in the coefficient of friction.

Based on a chemical analysis of the sample surface, it can be assumed that, in addition to a temperature increase, friction is also necessary to form a protective film on the surface.

The performed study shows that the influence of detergent additives (at least, calcium sulfonate) on the lubricating properties of oils is rather significant and it should be considered in the development of lubricant compositions.

The possibility of differentiation of oils for two-stroke petrol engines based on lubricating ability, and also on the detergency by means of a temperature method of an assessment of lubricating ability of oils is established.

In the set conditions the best thermal stability was shown by oil C on a mineral basis. Oils on a mineral basis of A and B have shown close thermal stability that suggest similar additive packages. Oil E on a synthetic basis has shown the greatest friction coefficient almost in all range of temperatures.

The visual assessment of mandrels after testing allows to evaluate the detergency of oils. Least of all traces of temperature influence when using synthetic oil E that will be coordinated with classifications of JASO and ISO.

REFERENCES

- [1] Dotsenko A.I., Buyanovskij I.A. Osnovy tribotekhniki. M: Infra-M, 2014. 335 s.
- [2] Meshcherin E.M., Ostrovskaya M.E. Oils for two-stroke petrol engines. Thematic review. – M.: TSNIITEHneftekhim, 1989. – 72 pp.
- [3] Igartua A., et al. Alternative eco-friendly lubes for clean two-stroke engines. Tribology International 44.6 (2011): 727–736.
- [4] Singh A. K. Castor oil-based lubricant reduces smoke emission in two-stroke engines. Industrial crops and products 33.2 (2011): 287–295.
- [5] Kumar G. S., Balamurugan A., et al. Tribological and emission studies on two stroke petrol engine lubricated with sunflower methyl ester. J Sci Ind Res 71 (2012): 562–565.
- [6] Matveevsky R.M., Lashkhi V.L., Buyanovsky I.A. et al. Lubricants. Antifrictional and antiwear properties. Test methods. – M.: Mashinostroenie, 1989. 192 pp.
- [7] ZHilko V.N., Buyanovsky I.A., Lisenkov Yu.G. About bond between temperature firmness of engine oils and their antiwear properties. Friction and wear T.4, № 4 (1983): 724–727.
- [8] Matveevsky R.M., Buyanovsky I.A., Karaulow A.K., et al. Transition temperatures and tribochemistry of the surfaces under boundary lubrication. Wear 136.1 (1990): 135–139.
- [9] Glavati O.L. Fiziko-khimiya dispergiruyushchikh prisadok k maslam. Kiev: Naukova Dumka, 1989.
- [10] Stachowiak G., Batchelor A.W. Experimental Methods in Tribology. Amsterdam, 2004.