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DISCUSSION AND STUDIES OF THE PROPERTIES OF A COOLING WATER ADDITIVE PREVENTING EROSIVE WEAR OF COOLED SURFACES OF SHIP DIESEL ENGINES

OPRACOWANIE I BADANIA WŁASNOŚCI DODATKU DO WODY CHŁODZĄCEJ ZAPOBIEGAJĄCEGO ZUŻYCIU EROZYJNEMU POWIERZCHNI CHŁODZONYCH OKRĘTOWYCH SILNIKÓW SPALINOWYCH*

This paper presents the results of studies on the properties of an additive administered into the liquid cooling a ship diesel engine. The protective action of the liquid relied on the formation of nickel layers on the cooled surfaces – electroless nickel plating of cooling surfaces. The test stand and the program of the experiment have been described. Statistical methods have been used for discussing the results. Regressive correlations of mass decrease of the studied samples, dependent on the conditions and the experiment program, have been obtained. Sample mass decrease was described as a function of the additive concentration, the flow and the temperature of the cooling liquid supplied by the pump. High effectiveness of the studied additive was presented comparing it with the substances widely applied for this purpose such as EKSTROL and NALCOOL-2000 basing on the verifying exemplary results. Validation of the obtained results carried out on real maritime technical facilities has been described.

Keywords: *erosive wear, cooling system, ship diesel engine, corrosion, nickel plating, regressive models.*

W artykule przedstawiono wyniki badań własności opracowanego dodatku do cieczy chłodzącej okrętowego silnika spalinowego. Działanie ochronne cieczy oparto na niklowaniu chemicznym – na bezprądowym tworzeniu warstw niklowych na chłodzonych powierzchniach. Opisano stanowisko badawcze oraz program eksperymentu. Do opracowania wyników przeprowadzonego eksperymentu zastosowano metody statystyczne. Otrzymano zależności regresyjne ubytku masy badanych próbek od warunków i programu eksperymentu. Ubytek masy próbek opisano w funkcji stężenia dodatku, strumienia objętości i temperatury cieczy chłodzącej, podawanej przez pompę. Pokazano wysoką skuteczność badanego dodatku w porównaniu ze stosowanymi do tego celu dodatkami EKSTROL i NALCOOL-2000 na przykładzie wyników badań weryfikacyjnych. Opisano walidację wyników przeprowadzoną na rzeczywistych obiektach oceanotechnicznych.

Słowa kluczowe: *zużycie erozyjne, układ chłodzenia, okrętowy silnik spalinowy, korozja, niklowanie chemiczne, modele regresyjne.*

1. Introduction

Corrosive and erosive damage to cooled surfaces of ship diesel engines, and in particular cooling surfaces of cylinder liners, significantly decreases their durability and overhaul life. The number of working hours of cylinder liners affected by corrosive and erosive action decreases to 50 % of their designed overhaul. Erosive wear of the coler of cylinder liner is often the cause of cracks [3, 4, 5, 10, 11, 14]. According to contemporary views, erosive damage develops in a cumulative way together with the progressing, with different intensity, mechanical damage which is the consequence of interaction of vibration cavitation, hydrogen brittleness and oxygen corrosion. Fig 1 shows erosive – corrosive damage to the cooling surface of a cylinder liner of a ship engine of the SULZER 8ZAL 40S type.

These processes develop due to cylinder liner vibrations beginning from mechanical piston interaction at the moment when the shaft goes through top dead centre, TDC and bottom dead centre, BDC. Generated vibrations of a cylinder liner in the cooling liquid create conditions which favour cavitation. Results of experimental studies on the analysis of damage on the outer surfaces of cylinder liners and occurrence of cracks under the coler of cylinder liner allow to conclude that for most types of ship diesel engines applied on ships total elimination of the processes of erosive-corrosive damage and that of crack formation, especially in four-stroke trunk-piston engines, is impossible [8, 13].

On contemporary cargo ship it is a common practice to use as improving additives the products of such companies like UNITOR Ltd. Netherlands, or Dieselguard NB, Rocor NB Liquid and Cooltreat AL. The first two products are liquid chemical compounds based on nitrites (or borates). They contain organic inhibitors of "typical" ferrous and non-ferrous metals. They are used in closed circuits of cooling water. A stable oxide coating, formed as a result of cooling water treatment, prevents electrolitic corrosion between metals of different potentials. As these products are alcaline in character, they eliminate acidic corrosion without having a negative effect on non-metal parts like sealings, glands, elastic leads, seals etc. They have a very important quality of maintaining the pH at a required level, even at their high dosages in the cooling water. However, there are limitations to their application when aluminium elements are used [9].

(*) Tekst artykułu w polskiej wersji językowej dostępny w elektronicznym wydaniu kwartalnika na stronie ***www.ein.org.pl***

Fig 1. Erosive – corrosive damage to the cooling surface of a cylinder liner of a ship engine of the SULZER 8ZAL 40S type

Cooltreat AL, a modern product of UNITOR - an industrial chemical company, is also an organic corrosion inhibitor with prolonged longevity, designed to be used in closed cooling water systems. Its advantage is ensuring corrosion protection to all materials used in engine cooling cycles. In contrast to other products it does not contain quickly useable components such as nitrates or sillicates. It was made on the basis of aliphatic acids. It is a totally organic and biodegradable product and thus it meets all the requirements of environmental protection.

Less commonly used are the products of such companies like PEROLIN or Drew Ameroid and EKSTROL additives produced by Centralnovo Nauczno-Issledowatelskovo Dizelnovo Instituta, Sankt-Petersburg Russia and NALCOOL-2000 manufactured by Detroit Diesel Corporation Power, Detroit, Michigan, USA. It is not due to their quality because of their more selective range of activity in a ship engine cooling system and in the availability in the world – at the place where the ship stays.

The presented examples of additives, which improve the properties of cooling water, currently used on cargo ships do not ensure complete protection of the cooled surfaces from damage. Organic additives based on oils, lowering the extent of erosive damage, have an adverse effect on rubber seals. On the other hand, inorganic additives protecting the cooled surfaces from corrosive damage do not protect from erosion. Therefore, the issue of ensuring durability of cylinder liners of ship engines becomes a complex task both from the point of view of lowering the vibrations of cylinder liners during engine operation and due to the necessity to ensure the resistance of cooled surfaces to the damaging effects of the cooling medium.

2. Requirements for additives improving cooling liquids for ship diesel engines

An analysis of effectiveness of the additives applied in cooling systems of diesel engines showed that their properties do not meet the expected requirements regarding protection from erosive-corrosive damage of cooled surfaces [8, 13]. Emulsifying additives, forming relatively durable thin protective layers, have, however, a destructive effect on rubber elements of seals. Inhibitor additives, remaining passive towards all the elements of the cooling system, form stable oxide layers on the protected surfaces, but the do not protect the surfaces from cavitation erosion. Therefore, development of a new additive, combining all positive qualities of the so-far used additives and without their faults, was necessary in order to protect the cooled surfaces effectively from corrosive-erosive wear [7]. An important property of such an additive is its ability to coagulate the nuclea of cavitation dissolved in the cooling liquid, with the consequence of degassing air baubles and sedimentation of hard particles [13].

However, during engine operation galvanic plating is not possible, whereas plating with nickel form the additive dissolved in the cooling liquid seems quite realistic, In contrast to galvanic nickeling, at chemical nickeling – nickel sediments on the protected surfaces without the use of an external electric field. The layer is formed as a result of the return of nickel ions from the solution due to the action of certain components of the solution. The recommended reductive components can be hydrazine, sodium hypophosphate or sodium borane [7] The main advantage of this method is that nickel sediments at a constant speed on the whole area of the cooled surface. Thin layers of nickel have a tendency to reflect the basic topography of the surface, whereas thicker layers give the effect of smoothing its topography. This fact is of extreme importance in the case of protecting cooling surfaces of engines with complex shapes and local erosive and corrosive contaminations. Coatings formed without using electrical current are characterized by good adhesion, plasticity, minute crystalline structure and also they have high resistance to corrosion and good mechanical properties. Taking into account the fact, that acidic environments are more aggressive in respect to ferrous metals, the developed additive shoud create a basic environment in the cooling liquid. A protective additive of the following composition: nickel sulphate, sodium hypophosphate, sodium citrate, sodium carbonate and also polyacryloamide as a surfaceactive additive has been suggested.

3. Laboratory stand and programme of research

Complexity of processes taking place in real condition of erosive wear of diesel engine elements makes it difficult to carry out research on identification of influence of particular factors on the intensity

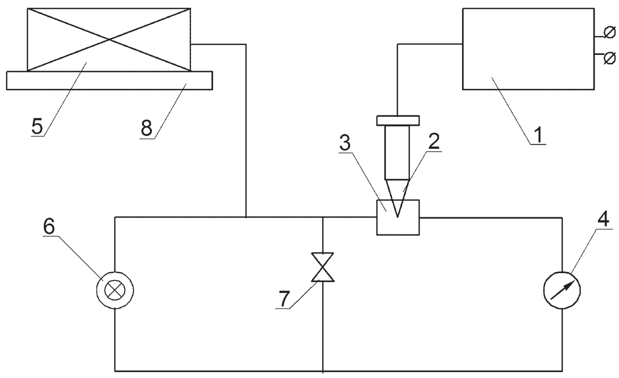

Fig 2. Laboratory stand diagram: 1 – ultrasonic vibration generator UZDN-1; 2 – magnetostriction vibration generator (vibrator) MSW-2; 3 – experimental cavitation chamber; 4 – flow meter LT-2-33; 5 – compensation container; 6 – circulation pump UPS 25-40; 7 – bypass valve; 8 – heating element

Table 1. Value ranges of independent parameters in the experiment

Parameters	Ranges of changes of parameter values			
	Reference	Change ranges	Lower limit	Upper limit
Additive concentration in the Solution C, %				
EKSTROL	0,3	0,2	0,1	0,5
NALCOOL-2000	3	2	1	5
PWTU – 2002	3	1	2	4
Cooling liquid volume flux, $\dot{Q}$, m^3/h	0,218	0,064	0,154	0,282
Cooling liquid temperature, t, ^0C	70	10	60	80

Table 2. Experimnet plan

No of experimental series	Level of parameter range		
	X_1	X_2	X_3
1	–	–	+
2	–	+	+
3	+	–	+
4	+	+	+
5	–	–	–
6	–	+	–
7	+	–	–
8	+	+	–

Table 3. Results of experiments performed in destilled water

Reading No	Parameter range level		Of active/passive sample mass loss [mg]				Standard deviation of the measurement
	X2	X3	m1	m2	m3	m4	S
1	-	-	5600/4150	5150/4050	5300/4150	5350/4120	132/32
2	+	-	5350/4200	5450/4300	5700/4350	5500/4280	104/44
3	-	+	5250/4600	5500/4300	5150/4750	5300/4280	104/132
4	+	+	5900/4050	5600/4550	5800/4250	5770/4280	88/145

Table 4. Results of experiments on effectiveness of solutions with NELCOOL-2000, EKSTROŁ i PWTU- 2002 additives

Reading No	Active/passive sample mass loss [mg], the negative sign for PWTU-2002 means mass increase											
	NELCOOL- 2000				EKSTROL				PWTU-2002			
	m_1	m_2	m_3	m_4	m_1	m_2	m_3	m_4	m_1	m_2	m_3	m_4
1	4050/150	3400/200	3800/200	3800/180	4952/1052	4152/800	4700/852	4600/900	-100/-700	-50/-550	-100/-1050	-83/-767
2	4150/150	4400/150	4400/150	4320/150	700/552	825/652	700/752	752/652	-100/-1150	-100/-1750	-100/-1750	-100/-1550
3	1950/350	1900/450	1550/300	1800/370	2052/100	2300/100	2100/100	2152/100	-100/-100	-50/-50	-50/-100	-67/-83
4	3150/200	2100/50	2550/50	2600/100	600/300	525/300	625/152	600/252	-100/-50	-100/-50	0/-50	-67/-50
5	4650/200	4400/150	5200/150	4920/170	4100/400	3900/400	3852/400	3952/400	-100/-400	-100/-900	-50/-750	-83/-683
6	4900/150	5100/150	4750/350	4920/220	3600/452	3400/400	4100/500	3700/452	0/-950	-100/-1200	-100/-800	-67/-983
7	3600/200	4000/300	3550/100	3720/200	3852/452	3100/300	2952/300	3300/352	-50/-100	-100/-100	-50/-50	-67/-83
8	2950/250	2700/250	3150/450	2930/320	3100/200	3352/252	3000/300	3152/252	0/-50	0/-50	-50/-50	-17/-50

of cavitation erosion. In a number of cases, wear caused by cavitation erosion is manifested within the long time of engine operation. Therefore, experimental studies on effective protective properties of PWTU-2002 additive were carried out as equivalent on a laboratory stand equipped in a magnetostriction vibrator. The vibrator imitated cavitation damage of a steel sample placed in a cavitation chamber at different parameters of the cooling medium flowing through the chamber. The studies were carried out in compliance with the GOST 30480-97 regulations – "Ensuring resistance to wear of goods. Methods of searching resistance to wear. Common requirements."[5], in compliance with PN-86/H-04427 regulation "Cavitation erosion. Vibration method studies on material resistance" [6]. Application of the analogue method of cavity phenomena studies was described in reference [2].

Studying protective properties of the PWTU-2002 additive, EKSTROL emulsifier and NALCOOL-2000 were used as reference. A diagram presenting laboratory stand is shown in Fig 2.

Laboratory studies were carried out on samples made of cast iron Scz24-36 grounded and degreased. Conditions of wear processes in cooling systems were modelled in experimental chamber (3) in which two samples had been placed: a passive and an active one. The active sample was tightly mounted on the head of the magnetostriction vibrator throughout a temporary screw joint which was a subject to lengthwise vibrations at 22 kHz. The gap between the active and passive samples was equal to 20mm which corresponds to the distance between the liner and the cylinder block (in the part that is washed by cooling water) of the engine 4 Cz 8,5/11.Studies were carried out for different compositions of additives in the cooling water and at their different parameters: form distilled water to a liquid with different additives such as PWTU-2002, EKSTROL i NALCOOL-2000. The value ranges of independent parameters, that were changed in the experiment are shown in Table 1.

Mass loss of both samples, after a single 4-hour measurement series, was the measure of additive effectiveness. Each experiment, repeated three times, was carried out according to the following procedure:

- electric heater was turned on and the circulation pump was set at maintaining a certain value of volume flux of the liquid;
- after the temperature has reached a required value and remained stable, an ultrasonic generator was turned on at 18 kHz frequency and the measurements were taken.

A set temperature was maintained during a single measurement series. Mass loss of a studied sample was determined using analytical balance WŁR- 200 g-M with the accuracy of up to $5x10^{-5}$ g. Plan of the experiment is shown in Table 2. To simplify notation in table 3 and 4 the following mean: $C=X_1$; $\dot{Q}=X_2$; $t = X_3$, (−) means the lower limit of the parameter, whereas (+) is the upper limit of the parameter and their values are given in table 1.

Examples of results for measurement series of different concentrations *C, [%],* volume fluxes $\dot{Q}$, *[m³/h]*and cooling liquid temperature, *t,* ^0C are given in Tables 3 and 4.

Values of standard deviations of mass loss results for both active and passive samples for the experiments carried out in the presence of NELCOOL -2000, EKSTROL and PWTU -2002 additives are shown in Table 5.

Accuracy of measurements was checked comparing the difference of the calculated values of the t-Student criterion with the listed in tables values of quantiles $[t_n(p_n)]$ for a given number of degrees of freedom and at an acceptable value of probability [1]:

$$t = \frac{[X^* - X_{sr}]}{S} \quad (1)$$

where: S –standard deviation of one measurement series,

X*– measured value, the most different from the mean value in a given series,

Xśr – mean value of the parameter for the considered measurement series.

Fulfillment of the inequality was a criterion of correctness of the checked value:

$$t > t_n(p) \quad (2)$$

The calculated Student criterion numbers for all measured values of mass losses in the carried out experiment indicated that they do not exceed the listed in tables t-Student distribution quantiles tn (p)= 3,182, for the experiment conditions: three degrees of freedom (X1, X2 i X3) and the assumed level of confidence p = 0, 95.

4. Processing and analysis of experimental results

The aim of processing of study results was to obtain regressive models whose applicability was checked using Fisher-Snedecor criterion. The obtained experimental results were processed and analysed using statistical methods. Calculations were performed with statistical means in Windows environment, whereas for their analysis the contemporary STATISTIC by StatSoft was applied. A model of the general type:

$$m = b_0 + Cb_1 + \dot{Q}b_2 + tb_2 + C\dot{Q}b_{12} + Ctb_{12} + \dot{Q}tb_{23} \quad (3)$$

was searched for, where C– concentration of the additive in the solution, $\dot{Q}$ – volume flux of the cooling liquid, t – temperature.

While preparing linear models of regression, determination of their coefficients was limited only to the effects of mutual interaction of two parameters/factors. The influence of higher order factors was not considered. With such an assumption the following regression models were obtained:

– for the active sample in a solution of EKSTROL additive:

$$m = 694 + 119C - 181\dot{Q} - 187t + 75C\dot{Q} - 44Ct - 156\dot{Q}t \quad (4)$$

– for the passive sample in a solution of EKSTROL additive:

$$m = 105 - 45C + 4{,}5\dot{Q} + 14t + 7{,}5C\dot{Q} - 30Ct - 1{,}5\dot{Q}t \quad (5)$$

– for the active sample in a solution of NALCCOL-2000 additive:

$$m = 3626 - 864C + 66\dot{Q} - 496t - 439C\dot{Q} - 66Ct + 264\dot{Q}t \quad (6)$$

Table 5. Standard deviations of mass loss of samples in the experiment

No	Standard deviation of the measurement (S)		
	NALCOOL-2000	EKSTROL	PWTU-2002
1	193/17	59/19	17/148
2	26/0	13/14	0/148
3	132/44	19/0	17/17
4	304/50	7/12	19/0
5	236/17	19/0	17/148
6	101/66	52/7	19/148
7	136/57	70/13	17/17
8	130/66	26/7	17/0

– for the passive sample in a solution of NALCCOL-2000 additive:

$$m = 214 + 21C - 16\dot{Q} - 14t - 21C\dot{Q} + 1,25Ct - 23\dot{Q}t \quad (7)$$

– for the active sample in a solution of PWTU- 2002 additive:

$$m = -69 + 14C + 6,13\dot{Q} - 10t + 6,38C\dot{Q} - 2,13Ct - 10\dot{Q}t \quad (8)$$

– for the passive sample in a solution of PWTU- 2002 additive:

$$m = -531 + 465C - 127\dot{Q} - 81t + 144C\dot{Q} + 81Ct - 60\dot{Q}t \quad (9)$$

These functions were searched for via the least squares method, whereas iteration processes were based on the quasi-Newtona method with the assumed criterion of convergence of calculated values with the experimental data of 0.05% of the values. In equations (4-9) the free term (b_0) determines the mass loss.

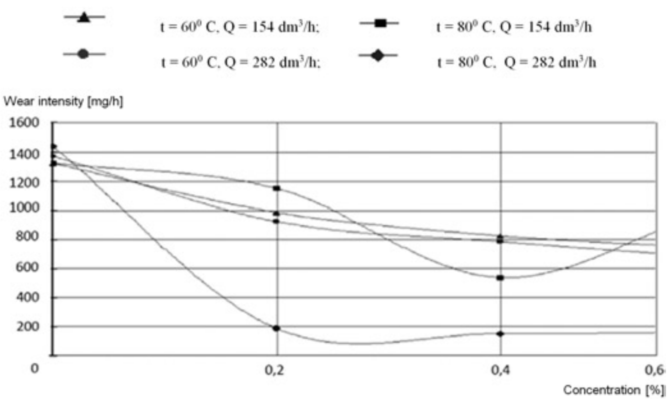

Fig 3. Active sample material wear intensity versus concentrations of EKSTROL additive

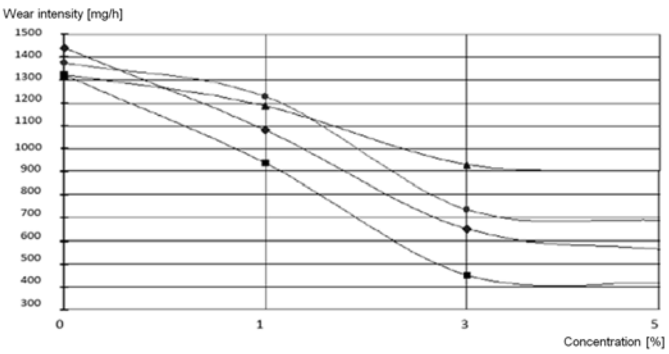

Fig 4. Active sample material wear intensity versus concentrations of NALCCOL-2000 additive

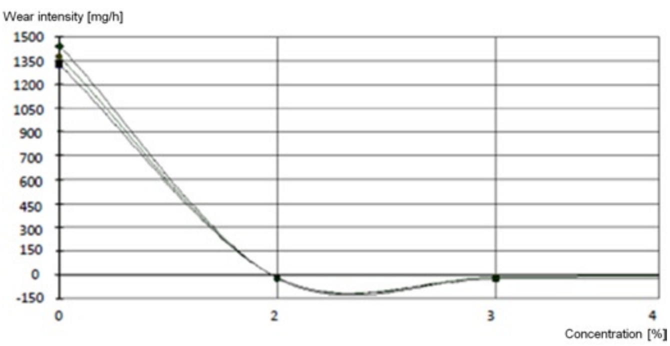

Fig 5. Active sample material wear intensity versus concentrations of PWTU-2002 additive

Thus, it is visible from the regression equations that the biggest mass losses both for the active and the passive sample occur in the solution of NALCOOL-2000 additive. Sample mass losses are smaller in the solution of EKSTROL additive, whereas negative values of the free term in regression equations for samples studied in the solution of PWTU- 2002 additive indicate sample mass increase as a result of formation of nickel coatings on their surfaces.

Signs of regression coefficients indicate positive or negative influence of the linear effect on the experiment result. In respect to various additives used in the study, it can be said that the influence of additive properties is different. It is the consequence of their very different physical and chemical properties. Figures 3, 4 and 5 present graphically the obtained models of intensity of wear of active samples, where different curves are ascribed to different experimental conditions:

Evaluation of experimental results at PWTU- 2002 additive concentrations in the range of 2 to 4% showed that mass of the samples increased on average by 83 mg. The surfaces, both of the active and the passive samples, became glossy, traces of corrosive – erosive wear disappeared. This effect is explained by formation of nickel coatings on the surfaces of the studied samples.

Mass decrease took place for the samples under the influence of magnetostriction vibration generator MSW in solutions of EKSTROL and NALCOOL-2000 additives. On their surfaces there were traces of corrosive –erosive wear in the form of shallow cavities in the central part of the sample and dark stains on the edges.

Analysis of curves in Fig 2–3 showed that the introduction of additives significantly lowers wear intensity of active samples. Optimal concentration of PWTU-2002 additive is 2,5–3 %, EKSTROL additive 0,4–0,5 %, and NALCOOL-2000 additive – 3,5 – 4 %. Further increase of concentrations did not affect mass wear intensity of the samples.

On the basis of relations shown in Fig 5 it can be noticed that increase of cooling liquid temperature up to 80° C as well as that of cooling liquid flux up to 282 dm3/h did not affect the properties of PWTU- 2002 additive. During the experiment increase sample masses and lack of wear cavities on their surfaces were observed.

Protective action of EKSTROL and NALCOOL-2000 additives decreased at small volume flux of the cooling liquid (154 dm^3 / h), which can be explained by the decrease of adhesive properties of additives with increasing temperature (figures 3 and 4). However, the increase of liquid flux up to 282 dm^3/h, which increases hydrostatic pressure, lead to a decrease of active sample wear intensity. It is explained by a delayed onset of the evaporation process and an increased resistance to cavitation at an increased water pressure in the system.

5. Summary

The result of the experiment was determination of coefficients in regression relations of mass losses for active and passive samples in the solutions of EKSTROL, NALCOOL-2000 and PWTU-2002 additives at different experimental conditions. Reliability of the obtained values of coefficients of relations describing the results of the experiment was determined with regression coefficients: for constant coefficients in the equations r = 0,99; for coefficients at linear parts r = 0,94–0,96 and for parts reflecting interaction of factors r = 0,89–0,90. Those values, throughout regression equations, confirm a good fit of the experiment model and justify generalizations.

Experimental laboratory studies on experimental samples and studies on industrial scale on ship diesel engines confirmed anti-erosive properties of the developed PWTU-2002 additive. The result of the study was an introduction of the additive into operation by recommending its application in cooling systems of ship diesel engines on seagoing ships.

Checking the anti-erosive properties of PWTU-2002 additive was carried out on industrial scale on ship diesel engines of the Sulzer 8 AL20/24 and 6 AL20/24 types, used as main and auxiliary engines on a vessel belonging to the Technological Management Fleet Łukoil-Kaliningradmornieft – a floating crane „Atlet-4". Two main and two auxiliary engines were cooled by a cooling system with a central cooler. An anti-erosive improving additive was introduced into the cooling system after mid shipyard overhaul of engines. During the process inner surfaces of the cylinder blocks were cleaned following a specially developed procedure. Verification of outer surfaces of cylinder liners was carried out during a subsequent current overhaul, after the main engines have operated for 244 hours and the auxiliary ones for 3500 hours. Organoleptic studies did not reveal any corrosive-erosive material wear, whereas a glossy nickel surface was observed.

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