

FTD-MT-65-319

FOREIGN TECHNOLOGY DIVISION



STRUGGLE WITH CORROSION IN PETROLEUM REFINING
INDUSTRY OF CZECHOSLOVAKIAN
SOCIALIST REPUBLIC

By

Sh. Korcheck and V. Vesely

Code 1

CLEARINGHOUSE
FOR FEDERAL SCIENTIFIC AND
TECHNICAL INFORMATION

Per copy Microfiche

\$1.00

\$0.50

23

pp

ARCHIVE COPY



APR 31 1966

57
APR 30 1966



This document is a machine translation of Russian text which has been processed by the AN/GSQ-16(XW-2) Machine Translator, owned and operated by the United States Air Force. The machine output has been post-edited to correct for major ambiguities of meaning, words missing from the machine's dictionary, and words out of the context of meaning. The sentence word order has been partially rearranged for readability. The content of this translation does not indicate editorial accuracy, nor does it indicate USAF approval or disapproval of the material translated.

DISTRIBUTION STATEMENT

Distribution of this document
is unlimited.

2	CLASSIFICATION	<input checked="" type="checkbox"/>
3	SECTION	<input type="checkbox"/>
4		<input type="checkbox"/>
5	AVAILABILITY CODES	
6	IL. and/or SPECIAL	

EDITED MACHINE TRANSLATION

STRUGGLE WITH CORROSION IN PETROLEUM REFINING
INDUSTRY OF CZECHOSLOVAKIAN SOCIALIST REPUBLIC

BY: Sh. Korchek and V. Vesely

English Pages: 21

SOURCE: Moscow. Vsesoyuznoy Mezhvuzovskoy Nauchnoy
Konferentsii Po Voprosam Bor'by S Korroziyey.
Trudy (Russian), 1962, pp 365-374.

Ref: S/0081-063-000-011

TT5502352

THIS TRANSLATION IS A RENDITION OF THE ORIGINAL FOREIGN TEXT WITHOUT ANY ANALYTICAL OR EDITORIAL COMMENT. STATEMENTS OR THEORIES ADVOCATED OR IMPLIED ARE THOSE OF THE SOURCE AND DO NOT NECESSARILY REFLECT THE POSITION OR OPINION OF THE FOREIGN TECHNOLOGY DIVISION.

PREPARED BY:

TRANSLATION DIVISION
FOREIGN TECHNOLOGY DIVISION
WP-APB, OHIO.

U. S. BOARD ON GEOGRAPHIC NAMES TRANSLITERATION SYSTEM

Block	Italic	Transliteration	Block	Italic	Transliteration
А а	<i>А а</i>	A, a	Р р	<i>Р р</i>	R, r
Б б	<i>Б б</i>	B, b	С с	<i>С с</i>	S, s
В в	<i>В в</i>	V, v	Т т	<i>Т т</i>	T, t
Г г	<i>Г г</i>	G, g	У у	<i>У у</i>	U, u
Д д	<i>Д д</i>	D, d	Ф ф	<i>Ф ф</i>	F, f
Е е	<i>Е е</i>	Ye, ye; E, e*	Х х	<i>Х х</i>	Kh, kh
Ж ж	<i>Ж ж</i>	Zh, zh	Ц ц	<i>Ц ц</i>	Ts, ts
З з	<i>З з</i>	Z, z	Ч ч	<i>Ч ч</i>	Ch, ch
И и	<i>И и</i>	I, i	Ш ш	<i>Ш ш</i>	Sh, sh
Й й	<i>Й й</i>	Y, y	Щ щ	<i>Щ щ</i>	Shch, shch
К к	<i>К к</i>	K, k	Ъ ъ	<i>Ъ ъ</i>	"
Л л	<i>Л л</i>	L, l	Ы ы	<i>Ы ы</i>	Y, y
М м	<i>М м</i>	M, m	Ь ь	<i>Ь ь</i>	'
Н н	<i>Н н</i>	N, n	Э э	<i>Э э</i>	E, e
О о	<i>О о</i>	O, o	Ю ю	<i>Ю ю</i>	Yu, yu
П п	<i>П п</i>	P, p	Я я	<i>Я я</i>	Ya, ya

* ye initially, after vowels, and after ъ, ь; e elsewhere.
 When written as ѣ in Russian, transliterate as yě or ě.
 The use of diacritical marks is preferred, but such marks
 may be omitted when expediency dictates.

MT-65-319

Transactions of the All-Union
Inter-University Scientific
Conference On Questions of
Struggle With Corrosion.
Moscow, Gostoptekhizdat, 1962.
Pages: 365-374

STRUGGLE WITH CORROSION IN PETROLEUM
REFINING INDUSTRY OF CZECHOSLOVAKIAN
SOCIALIST REPUBLIC

Sh. Korcheck and V. Vesely

Slovak Institute of Technology
(Bratislava)

Systematic struggle with corrosion in the petroleum refining industry of Czechoslovakia (ChSSR) started relatively recently, in connection with the transition of petroleum refineries to new raw material-oil of Volga-Ural region of USSR. Earlier in Czechoslovakia was refined oil of Rumania, Hungary, Austria, and also domestic oil, mostly low-sulfurous or in general, without sulfur. Only in 1948-1949 during brief refinement of Kuwait oil was phenomenon of corrosion observed. During thermal cracking for one month, there occurred wear of furnace pipes and return bends made of carbon steel, to the thickness of paper. A proposal of the firm UOP (Chicago) to remove corrosion by means of addition of calcium hydroxide into the raw material was impossible to carry out since it was necessary to observe technical conditions related to the ash content for petroleum coke. They refined Kuwait oil for a comparatively short period; therefore, it was impossible to accumulate great experience related to the struggle with

corrosion.

During atmospheric and vacuum rectification of petroleum with a low-sulfur content, only insignificant corrosion was observed; carbon steel in the furnace, and in heat exchangers was satisfactory.

Corrosion, caused by hydrogen chloride, was observed in the upper part of atmospheric tower and mainly in heat exchangers. For the struggle with this type of corrosion, ammonia was introduced into the side and upper part of the atmospheric tower until condensate was obtained in an pH-7 gasoline capacitor. Corrosion was determined by the state of metallic plates, installed in the upper part of atmospheric tower. Plates were prepared from 18-8 stainless steel, carbon steel, copper, aluminum, lead, and tin. Best results were obtained for stainless steel, whose corrosion rate was below $0.1 \text{ g/m}^2 \text{ hour}$. Tin gave good results (below $0.1 \text{ g/m}^2 \text{ hour}$). Then follow carbon steel and lead ($0.1-1 \text{ g/m}^2 \text{ hour}$).

In vacuum tower and heat exchangers, considerably less corrosion is noted under the influence of naphthenic acids, mainly during refinement of Rumanian oils. The introduction of ammonia in the vacuum tower did not give perceptible results.

The most effective method of the struggle with corrosion was desalting of petroleum. Certain petroleum possessed a high content of chlorides. For example, Rumanian paraffinaceous oil/^{of}Gura Oknitsei contained up to 2000 mg/liter of chlorides in conversion to sodium chloride. Desalting was produced with the help of Swedish separators of brand de Laval with 1400 rpm. The content of salts was possible to lower to 120 mg/liter NaCl, and sometimes to 50 mg/liter NaCl, mainly with the addition into oil of de-emulsifiers of green sulfonate type. Gradually they turned away from the application of separators,

since they wore out rapidly and gave very dirty sewage, which is impossible to drain into a sewer. Furthermore, they turned out to be useless when desalting Soviet oils. Certain plants temporarily conducted desalting with the help of glass fibers according to experience/^{of}/many Rumanian plants, improved by the application of de-emulsifiers. At present in connection with development of desalting process in USSR and in the entire world, our plants transfer to electrostatic desalting, which is preceded in our production by thermochemical treatment.

While refining Saratov and Mukhanovo oils, desalting did not bring any difficulties and completely satisfied inexpensive de-emulsifiers Dubosol (sodium salt of water soluble sulfonic acids — waste in production of white liquid petrolatum product, analogous to NChK). But while refining Romashkinskiy oil, this de-emulsifier turned out to be unsatisfactory. During electrostatic desalting with preceding thermochemical treatment there was attained only small desalting effect; together with water was lost a considerable quantity of emulsion. Even a raised dosage of de-emulsifiers did not help. Searches of new effective de-emulsifiers were directed towards investigation of substances, widely-spread in Czechoslovak SSR, for which according to chemical structure was assumed high effectiveness.

Attention was turned chiefly to unionogenic de-emulsifiers products of condensation of fatty acids and alcohols with ethylene oxide (slovasol O, slovasol YeL, slovasol S, slovaviv SG-100, and slovaviv SG-50), and cation-active de-emulsifiers (kateksol 319 and 298). Their chemical composition is shown in Table 1.

Table 1

De-emulsifier	Chemical composition
Dubosol	Sodium salt of water-soluble sulfonaphthene acids.
Dubosol	Ammonium salt of the same acids
Dubarol	Alkylarylsulfonate
Slovasol 0	Polycondensate of mixture of oleic and cetyl alcohols with ethylene oxide.
Slovasol YeL	The same-ricinic oil
Slovasol S	The same-lauryl alcohol
Slovaviv ST-100	The same-stearic acid
Slovaviv ST-50	The same
Kateksol 298	Laurylamidoethylpyridinechloride
Kateksol 319	Laurylamidoethylpyridinesulfate
Separol 22	High-molecular surface active organic substances of unionogenic character.
Separol 221	The same
Separol 11	The same
Dissol'van 4400	Polyalkyleneglycols
Dissol'van 4411	The same
Dissol'van 4422	The same
Dissol'van 4433	The same
OP-10	Alkylphenols
Kaufe 14	

Above mentioned substances were compared according to effectiveness with de-emulsifiers of brand Separol and Dissol'van (FRG), and also with de-emulsifiers OP-10, Kaufe 14 (USSR). In the process desalting of Romashkinskiy oil, good results were attained during application of de-emulsifiers slovasol 0, slovasol YeL, and kateksol 298 and 319. The latter, with dosage of 40 g in 1 t, in single-step electrostatic desalting with preceding thermochemical treatment gives a good desalting effect. Quantity of salts becomes lower than 30 mg/liter. Laboratory and industrial investigations have shown that above mentioned domestic de-emulsifiers are not inferior, with respect to effectiveness, to de-emulsifiers produced in FRG (in production for

us were conducted experiments only with Separol 22 de-emulsifier). By laboratory tests it is established that effectiveness of the given de-emulsifiers is approximately 40% higher than for Soviet de-emulsifiers. From appraisal of industrial tests it follows that as a result of the introduction of a new type of de-emulsifier, expenditure of chemicals was lowered by 3 times as compared with dubosol. From the number of studied de-emulsifiers, into production in the Slovnaft plant was introduced slovasol O. The above-mentioned achievements in the area of desalting of Romashkinskiy oil on the basis of new de-emulsifiers are the result of investigations of Eng. K. Trubach from the Central Laboratory of the Slovnaft Plant in Bratislava.

Another cause of corrosion is sour compounds of oil. It is known that sour crudes unequally corrode metal. The degree of corrosion depends on what compounds of sulfur are contained in oil. Oils are known, which despite considerable content of sulfur are weak-corrosional. Oils of the Volga-Ural region, processed in our plants, pertain to oils of corrosional type. Romashinskiy possesses the greatest corrosional properties.

Introduction of ammonia is already insufficient for them; therefore, attention was paid to so-called film-forming inhibitors of corrosion. At present we have studied inhibitors of canarad type (producer Canadian Aniline Co, Ltd., Ontario) and Sepakorr (producer BASF, FRG). Both inhibitors are high-molecular polyamino-compounds with one or more hydrophobic groups. Basic properties of canarad:

Specific weight	0.981
Color	yellow
Fractional composition:	
initial.	80°C
30%.	90°C
40%.	110°C
50%.	270°C
70%.	305°C

Thermal resistance: according to prospect 250°C, at a temperature higher than 280°C was noted decomposition of inhibitor, with yield of gaseous substances of caustic odor and change of color (blackens).

Properties of both applied inhibitors in detail are studied in VURUP (Bratislava) by Eng. P. Koshtur in connection with difficulties during dissolution of inhibitor in gasoline. There solubility in water, Romashkinskiy gasoline, solvents, widely applied during processing of oil, and the behavior of these solutions at low temperatures were checked. For pipe installations, the most economic is a dosage of canarad solution in gasoline 1:1, which is suitable even in winter.

Into production we started to apply canarad in May 1959, when we revealed large corrosion of equipment of pipe installation. Following objects are mostly subjected to corrosion: top of atmospheric tower, upper pipelines, reflux pipelines, reflux pumps (ring, valves, springs), heat exchangers and collections for gasoline.

At first the solution of inhibitor (~12 liter) was introduced into the upper part of atmospheric tower, we assumed that one part of inhibitor passes ^{into/} the upper pipeline, other — into the tower every 8 hours. This corresponds to an expenditure of inhibitor about 10 kg per day. Effectiveness of inhibitor was determined by value pH and content in condensate. Upto the dosage of canarad (without addition of ammonia into the tower) concentration Fe in condensate composed 1500 ml/liter, and pH about 2. After introduction of

canarad, content of Fe dropped to 300 milligram/liter, and after an additional introduction of ammonia -- to 60-100 milligram/liters, when pH was changed from 6 to 10.

The decrease of corrosion is possible to indicate by life of valves and valve springs of reflux steam pump, increasing from 10 days to 3 months. Later, these valves, prepared from cast iron or bronze, were replaced by valves from polyamide material and well proved their value.

During the above-indicated method of introduction of inhibitor, it was not known, how much of it gets into the tower and into the upper pipeline. There could be insufficient protection of upper pipeline, heat exchangers, and collection. Therefore, they began to introduce inhibitor into the upper pipeline at a distance of approximately 30 cm from the wall of the tower as a result of which was ensured protection up to the collection itself. The tower was protected by inhibitor, introduced into it with reflux gasoline. Expenditure of inhibitor composed 0.001 % by weight, considering raw material.

Effectiveness of inhibitor in the pipe installation is evaluated with the help of control samples of steel 11 107 (C = 0.12 %) of following dimensions: diameter 15 mm, length 125 mm. Degree of destruction of equipment from corrosion was determined by decrease of weight of samples, expressed in g/m^2 per day.

With the help of a special device, control samples are placed in designated places of installation during the industrial process. Such device was on pipe installations of all Czechoslovakian oil refineries.

In Slovnaft plant (Bratislava) it was installed in upper part of atmospheric tower, upper pipeline of atmospheric tower -- over heat exchanger, connecting vent between heat exchanger and refrigerator,

lower part of water separator — in water layer.

On a pipe installation of OSTRAMO plant in Ostrava, this device was installed in upper part of atmospheric tower, upper pipeline of evaporative tower, upper pipeline of vacuum tower, atmospheric condenser — between first and second condenser of upper product. In the Slovnaft plant samples were tested for five cycles, each of which continued three weeks. Two cycles were conducted without inhibitor, three — applying inhibitor. Unfortunately, results of separate cycles are oscillating, since the content of salts in oil was strongly changed (average data calculated for separate cycles oscillate from 60 to 90 milligram/liter), and pH of water also changed (from 4 to 9.5). Cause of oscillation of results were interruptions in the dosage of inhibitor.

It is possible to affirm that the degree of destruction of equipment from corrosion considerably dropped thanks to application of inhibitors.

Experiments will continue at constant conditions, when pH of waters will be supported by constant registration-regulating apparatus for dosage of ammonia; dosage of inhibitor will be continuous.

In the Slovnaft plant corrosion is observed on the installation of thermal cracking, mainly in gasoline refrigerators, where most of all pipes bringing gasoline into the inlet to the refrigerator are destroyed.

For decrease of corrosion the following measures were accepted:

a) on the refrigerator inlet was inserted a pipe of large diameter stainless steel;

b) according to experience of pipe installations, into the fractionating column was introduced ammonia and into the upper pipeline was added inhibitor canarad.

On the installation of oil deparaffination during application of solvent of system barisol the corroding substance is dichlorethane, which at temperatures higher than 140°C is decomposed with isolation of HCl. This can be the cause of intense corrosion. If reclamation of solvent is produced at a temperature not higher than 130°C and steam with pressure 8 atm (tech.) superheated to $\approx 230^{\circ}\text{C}$ is used for preheating, then corrosion does not obtain dimensions threatening uninterrupted movement of production. Condensers of humid barisol are the most subject to corrosion; duration of operation of pipes from carbon steel (class 11) is not less than three years. Metal pulverization of heat exchanger pipes with copper turned out to be unsuitable because of insufficient cohesion of copper with steel. In fractionating columns raised corrosion is not noticed, but despite this in 1960 they started to introduce ammonia into the upper pipeline. The life of collections for barisol and mixtures containing barisol composes 10 years.

On the installation of oil purification by selective solvents (type duosol), a change of content of hydrogen sulfide and hydrogen chloride in phenol waters and gases distillation at low pressure was observed. In phenol waters was revealed 46.7 milligram/liter of chlorides; sour ions are not found. Hydrogen sulfide content in gases composed 2.6 milligram/liter and hydrogen chloride — almost 20 milligram/liter. These data show that during selection of method of protection from corrosion of installation duosol in case of imperfect desalting, it is necessary to consider combined ^{corrosion/}by hydrogen chloride and hydrogen sulfide.

The concept on behavior of steel, aluminum, and brass in condition of purification of oils by phenol and cresol can be obtained from results of laboratory experiments (see Table 2).

During application of aluminum pitting was observed. During experiments we studied only the influence of pure solvents. Furthermore, it is necessary to consider corrosion during action of extracts.

Table 2

Medium	State	Corrosion rate, g/m ² hour.		
		carbon steel	aluminum	brass
Boiling phenol	vapor	0.01	0.00	0.12
	liquid	0.36	0.03	0.44
Boiling cresol	vapor	0.01	0.03	0.30
	liquid	0.03	0.01	0.09
Boiling phenol water	vapor	0.29	0.01	0.18
	liquid	0.12	0.02	0.05
Boiling cresol water	vapor	0.08	0.05	0.09
	liquid	0.02	0.02	0.12

During contact purification of oils by bleaching clays of Czechoslovakian production (from Hungarian raw material), there appeared strong corrosion of tower, heat exchangers, and pumps. (Period of service of the tower of contact purification is approximately 2 years.) Therefore in VURUP and Central plant laboratory OSTRAMO, main attention was turned to investigation of corrosion in the tower during contact purification.

The above organizations placed before themselves the target of qualitatively and quantitatively determining the presence and aggressiveness of gaseous components during experiments, simulating industrial contacting. In gaseous products they determined mainly hydrogen sulfide and hydrogen chloride, which promote corrosion of equipment. Hydrogen sulfide appears at a temperature around 180°C and its quantity

grows with an increase of temperature, with an increase of time of contacting, with an increase of quantity of bleaching clay, and becomes large during the application of corrosional clays.

In broad terms it is possible to say the same about the second aggressive gas - hydrogen chloride, which is obtained from bleaching clay. Hydrogen chloride is emanated at all investigated temperatures from 130 to 250°C, but its dependence on studied parameters is not so regular as for hydrogen sulfide. (Problem of clays we will consider further.) Corrosion of equipment is increased with an increase of temperature, about which it is possible to indicate by an increase of quantity of products of corrosion. Conversely, corroding properties of prepared oils drop with an increase of temperature. Therefore, in production the operating temperature was lowered from 250 to 220°C, dosage of ammonia was introduced, and application of inhibitors was planned.

On the installation of contact purification of oils will be also mounted a device for installation of control samples. Till now was observed only the content of Fe (on the average of 1.2 milligram/liter for pH water (from 6 to 8)).

Enumerated methods of the struggle with corrosion would be incomplete if one did not recall that in almost all productions the behavior of different structural materials (steel, other metals, plastics) and their resistivity to corrosion in a given medium are investigated. This is carried out by means of installation of plates or samples in sections of interest to us. Also different coverings protecting from corrosion reservoirs, acid mixers, etc., are investigated.

In KORAMO and Slovnaft oil refineries, the G. V. Akimov Scientific Research Institute of Metals Protection (SVUOM) conducts these investigations. Chemoproject investigates corrosion resistivity of metallic materials in rectification installations (plant PARAMO).

Above was discussed corrosion of equipment during processing of oil and its products; further we will stop on the question about corroding properties of certain products and protection from corrosion.

During the correct method of oil processing, gasoline cannot be corroding, even if they obtain it from sour oils. This pertains to gasoline purified by sodium plumbite, and to the most wide-spread type of gasoline, obtained in pipe installations and during thermal cracking. During careless purification by sodium plumbite (if gasoline is in the presence of H_2S for a long time, an excessive quantity of sulfur), gasoline can become corroding, mainly with respect to copper.

It is established that it is possible to lower these corroding properties by addition of anthranilic in gasoline, possessing, furthermore antioxiizing action and the ability to lower activity of metal. A similar property of anthranilic acid (in quantity of 0.005-0.02%) appears in corrosional kerosene and diesel fuel.

For diesel fuel sulfurous corrosion caused by products of combustion is very dangerous. With this form of corrosion is conducted the struggle, mainly with the help of additives in lubricating oils. In ChSSR were developed complex additions on the basis of sulfonaphthenates of calcium with excess of alkali, combined with dialkyldithiophosphate (VURUP), promising good results. In connection with hydrogenation of a considerable quantity of diesel fuel, one should expect a decrease of its corroding properties.

Problem of vanadium corrosion of black oil is solved in VURUP (Eng. Svrshchek), where several inhibitors of corrosion were prepared which were checked on a laboratory installation for 100 hours. The basic fuel during this was black oil, containing 53.8 mg vanadium and 25.2 mg sodium in 1 kg of fuel. Test samples were prepared from steel AKTs (chrome-nickel austenite, fire-resistant to 1100°C).

Colloid inhibitor K-S, containing 5.77% Mg and 1.175% Si is prepared and studied. Silicon was added in the form of tetrabutoxysilane for the purpose of lowering the formation of sediments. Inhibitor K-S was measured out to fuel in quantity representing molar ratio Mg:V = 6:1.

First of all was compared the action of inhibitor K-S with another inhibitor (Mg-naphthenate with ratio Mg:V = 6:1). Effectiveness was determined on the basis of experiments with initial black oil (without inhibitor) and with deasphalted deparaffined heavy oil from Saratov petroleum (K-460) with an insignificant content of vanadium. All experiments were conducted at a constant temperature of 750°C. Results are shown in Table 3.

Table 3

Type of Fuel	Corrosion	Sediments
	mg/cm ²	
Black oil	34.5	29.5
Oil K-460	7.3	7.9
Black oil with Mg-naphthenate . .	6.7	9.8
Black oil with inhibitor K-S . .	6.0	7.7

From Table 3 it is clear that inhibitor K-S is better than Mg-naphthenate. At these additives and at 750°C, the quantity of sediments and corrosion turns out to be the same as in oil K-460. Corrosion was lowered by 79%, and quantity of sediments — by 67.5% in comparison with black oil without an inhibitor.

Subsequently they checked the action of inhibitor K-S at various temperatures (Table 4).

Table 4

Temperature, °C	Corrosion	Sediments
	mg/cm ²	
655	3.3	2.9
750	6.0	7.7
805	7.4	9.6
852	24.3	26.6

Inhibitor K-S up to a temperature of 805°C substantially lowers corrosion and the formation of sediments to the degree observed for oil K-460. At 850°C the inhibitor somewhat lowers corrosion and the formation of sediments in comparison with black oil without inhibitor (at 750°C), but to an insufficient degree. One can make the conclusion that inhibitor K-S up to 805°C prevents vanadium corrosion and the formation of sediments.

They also checked the second inhibitor at temperatures of 650, 750, and 850°C (Table 5).

Table 5

Type of fuel	Temperature, °C	Corrosion	Sediments
	mg/cm ²		
Black oil with inhibitor (at molecular ratio Mg:V = 6:1)	650	1.7	3.2
	750	2.8	4.0
	850	10.7	10.9
Black oil with inhibitor (at molecular ratio Mg:V = 3:1)	650	2.7	3.8
	750	5.3	6.7
	850	10.3	10.8
Black oil	650	25.4	19.2
	750	34.5	29.5
	850	30.6	23.5
Oil K-434	650	2.2	2.2
	750	2.5	4.0
	850	4.9	3.3

Besides colloid hydrate of magnesium oxide, inhibitor contained colloid silica gel. This inhibitor was compared from the viewpoint of formation of sediments and corrosion with initial black oil and deparaffined moderate distillate from Sarotov oil (K-434). From comparison of results it is clear that this inhibitor, added in a quantity corresponding to the molar ratio $Mg:V = 6:1$ lowers corrosion and the formation of sediments at $750^{\circ}C$ to the same dimensions as during the application of moderate distillate. It is possible to say that for turbines of internal combustion and boilers working at high temperatures, it is possible to apply black oil with an addition of inhibitor instead of distillates.

Laboratory samples of the new inhibitor were prepared on the basis of colloidal hydroxide of zinc, which after its addition into black oil in quantity of $Zn:V = 6:1$ made it possible to increase temperature to $982^{\circ}C$. The same inhibitor, still containing colloidal silica gel, increases temperature to $978^{\circ}C$, i. e., approximately $160^{\circ}C$ higher than during usage of the most effective magnesium inhibitors. Investigations of these inhibitors continue.

For lubricating oils there appeared special corroding properties, obtaining during purification by their bleaching clays. In connection with this were studied the influence of temperature, time of contacting and quantity of clay on the bleaching effect of oil, and the quantity of hydrogen sulfide and hydrogen chloride emanated from clay (as we noted earlier) on the corroding properties of oils.

These dependences and properties were investigated on the following clays: 1) noncorrosional clay — NZ_N , prepared in Bratislava from Hungarian raw material — Butateteny; 2) corrosional clay — NZ_K , prepared in Bratislava from Hungarian raw material — Istenmexo.

Chemical composition of these clays is given in Table 6.

Table 6

Clay	Content %							
	SiO ₂	P ₂ O ₅	Al ₂ O ₃	Fe ₂ O ₃	MgO	S	in aqueous extract	
							SO ₄	Cl
NZ _N	65.29	17.40	16.55	2.85	0.35	0.04	0.33	0.24
NZ _K	73.36	13.59	12.21	1.38	0.65	0.04	0.35	0.23

These clays possess the following properties:

	NZ _N	NZ _K
Acidity, % HCl.	0.03	0.03
Humidity (drying at 150°C), %.	8.77	7.35
Loss during heat treatment, %.	12.57	10.37
Adsorptive power, ml of toluene/100 g.	4.85	4.60
Surface (S), m ² /g.	130.3	137.4
Volume of pores (V), cm ³ /g.	0.339	0.336
Average radius of pores 2V/S, A	48.7	32.0

Corroding properties of oils, obtained with purification by bleaching clays, with respect to copper and steel were studied by experiments for 12 hours at 110°C. During application of oil unpurified by clays, and purified by clay NZ_N in experiments, was proven that they are not corroding. Experiments with clay NZ_K at different temperatures showed that corroding properties of oils drop with an increase of temperature. Oils obtained by purification at low temperatures (90-150°C) are more corrosionally dangerous than oil obtained by purification at temperatures above 180°C, which scarcely corrode or generally do not corrode. Additions of ammonia and canarad do not render any influence on corroding properties of purified oils.

In connection with the fact that corrosiveness of oil is caused by clay NZ_K, they began to look for corroding substances in it. They extracted clay NZ_K with the help of benzene and tested the obtained

extract on corrosiveness. A copper plate immersed in benzene extract became black already after half an hour. In this extract was revealed 0.003% S (in conversion to weight of clay). Clay NZ_K itself during prolonged heating emanates H_2S (0.005%). During purification of oil by bleaching clays, sulfurous substance is extracted by oil from clay and with that promotes an increase of its corrosiveness. It was revealed that during heating of clay above $200^{\circ}C$, corroding sulfurous compound is decomposed.

Since plant-producer cannot remove corrosiveness of clay by heating above $200^{\circ}C$, then thorough control for the production process is necessary in particular, electric insulating oils (corroding substance causes corrosion of copper and increases the angle of electrical losses).

Plant-producer should give large consideration to washing of clays, as a result of which their acidity drops.

It is noticed that corroding properties, caused by application of unsuitable clays, are possible to completely remove by addition of small quantity (0.01-0.02%) of anthranilic acid.

Usually it is required so that lubricating oils would be non-corroding, and some, furthermore, would possess the ability to protect surfaces from corrosion influence of the medium. This protective ability is necessary, for instance, in steam turbines, frequently ceasing operation, in which the film of oil should protect metallic surfaces from action of water and other aggressive substances.

In ChSSR turbine oils were prepared earlier from Austrian raw material — Mashchenskiy oil. During transition to Saratov oil, it was necessary to increase the depth of purification in order to obtain oil with the same resistance to aging as for oils from Mashchenskiy

raw material, and to add antioxidants to them (2,6-di-tert-butyl-p-cresol).

Problem of protectivity of these oils was solved in oil-refining plant in Ostrava (Eng. Mashek, Vecnerka, Dragoun) and in the department of oil, processes, and apparatuses of SVShT in Bratislava. They started from experimental introduction into exploitation of oils, containing 0.02% anthranilic acid as a unit of complex addition (antioxidant, anticorrosive, and protective). These oils give good results in field testing first of all where a small quantity of water penetrates into oil (anthranilic acid is partially dissolved in water).

Study of protective properties according to method ASTM-D-665-54 has shown that anthranilic acid essentially improves these properties, and water corrosion of standard carbon steel rods is very insignificant. Better results were obtained in the laboratory according to method ASTM with oils containing, besides 2,6-di-tert-butyl-p-cresol (0.15%), anticorrosive addition Santolube AR of the Monsanto firm than with anthranilic acid. In this case in general, no corrosion is noticed. Oils with addition of Santolube in ChSSR are widely prepared and are investigated in conditions of production. Study continues in laboratories.

Conclusions

1. Investigations conducted in ChSSR and USSR showed that the most essential condition of lowering corrosion is deep desalting of oil. In heavy conditions of desalting (Romashkinskiy oil), nonionic de-emulsifiers turned out to be more profitable. It seems to us that the problem of selection and application of suitable de-emulsifiers is necessary to solve jointly in the frames of the Council of economic mutual assistance (SEV).

2. During processing of sulfurous oils one should select materials, resistant to corrosion by sulfurous compound. In the process of work on old equipment from carbon steel, corrosion is lowered by means of introduction of so-called film-like inhibitors of corrosion into steam outgoing from distillation installations. Meanwhile there are /only preliminary results indicating lowering of corrosion of loaded components and component parts during the use of inhibitors. We reason that in the given area a wide exchange with experience and an attempt of joint solution of these questions in the frames of SEV are necessary.

3. World and domestic experience of the struggle with corrosiveness of petroleum products shows that the most perspective is the means of application of suitable additives. Experiments in this area are conducted in ChSSR chiefly in laboratory scales. From first experiments the most interesting are with colloidal additions against vanadium corrosion, and with complex additions of the anthranilic acid type.

Literature

1. Ľ. Stehlik, Ropa a uhlie, 2(10), No. 10, 303-307, 1960.
2. M. Marko, V. Mašek, R. Poštulka, and V. Veselý. I, Ropa a uhlie, 1(9), No. 4, 104-108, 1959; II 1(9), 168-179, 1959.
3. J. Dragoun and M. Večerka. Ropa a uhlie, 2(10), No. 5, 146-148, 1960.
4. V. Mašek. Ropa a uhlie, 2(10), No. 5, 149-151, 1960.
5. V. Pallo, J. Prokeš, and V. Mašek. Elektrotechnický obzor, zv. 46. c.5.