zation. For this reason, there are fewer cases of ignition of automobile gas cylinders than gasoline tanks.

The isolated cases of ignition of gas cylinder ZIL-138A vehicles are due to the design of the gas apparatus, which allows leakage of gas in formation of hydrate vapor locks in the medium-pressure gas line (from the unheated high-pressure regulator to the low-pressure regulator) to the exhaust pipe zone. In a gas fuel apparatus with one pressure regulator located in a well ventilated space under the hood where there are no highly heated parts, these leaks do not take place and ignition is not observed.

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PRODUCTS OF OIL SHALE REFINING FOR THE MANUFACTURE OF SLUSHING MATERIALS

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UDC 662.73:621.892

The means of temporary corrosion protection that are in use at the present time – oil-soluble corrosion inhibitors, slushing and lubricating/slushing oils and greases, and also film-forming inhibited compounds – are manufactured mainly from petroleum feedstock. The stabilization in oil production that has been seen in recent years, the depletion of traditional fields, the deterioration in the quality of produced oil, and the increase in cost of petroleum products have resulted to a significant degree in the shortage of slushing materials in the national economy. In addition, mineral base oils (M-11, MS-20, etc.) and industrial oils that are intended for other purposes are being used for the production of slushing materials, firstly slushing oils.

As a result, there is now a need for alternative sources of feedstock for the production of slushing materials. In particular, the use of the products of the refining of oil shales as components of slushing materials appears to hold promise. The main field that is of interest for industrial processing is in the Baltic basin; around 95% of produced shale come from it [1]. The technology of oil shale refining consists of thermal decomposition in chamber furnaces and gas generators to produce shale tar and high-energy gas. The mixture of shale tars from the gas generators and chamber furnaces is distilled in an atmospheric rectification column to produce the following fractions: gasoline fraction, diesel fraction, light and heavy residual fuel oils.

We have investigated the possibility of expanding the raw material base for the production of slushing materials by using shale tar, its distillates, and also commercial products produced from them. With consideration of contemporary shale refining technology, generator tar of typical blended composition and two industrial fractions of atmospheric distillation of shale tars (230-320 and 320-360°C) were selected for investigation. Tar produced in vertical chamber furnaces for semicoking of shale with subsequent pyrolysis of the vapor-gas mixture at 650-700°C was tested for comparison.

Shale tar and its distillation products have low pour point and viscosity at the level of the oils that are used for manufacture of slushing compounds (Table 1). Fairly high ini-

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TABLE 1

Characteristic	Shale tar		Fraction, °C	
	gas generator tar	chamber tar	230—320	320—360
Density at 20°C, kg/m^3	1014	1044	991	1025
Viscosity at 50°C, mm^2/sec	11	14	20	70
Group composition, wt. %				
hydrocarbons	55	65	67	40
neutral oxygen compounds (NOC)	21	15	17	26
phenols	24	20	16	34
Temperature, °C				
initial evaporation point	—	—	102	146
pour point	—20	—	—30	—26
oxidation temperature	—	—	212	265
Molecular weight	287	235	220	253
Elemental composition, %				
carbon	82,5	82,3	83,7	80,4
hydrogen	9,3	8,3	11,6	9,5
sulfur	0,7	0,8	0,7	0,7
oxygen	7,5	5,7	5,8	10,1

TABLE 2

Sample	First signs of corrosion, cycles				Surface damage (HBr displacement, 4 h), %
	G-4 heat and humidity chamber	sulfur dioxide chamber	HCl mist chamber	immersion in sea water	
Slushing oil K-17	48	0,9	3,0	25	50
AKOR-1 (25%) in M-8 oil	30	0,8	0,9	5	60
Tar					
gas generator	35	0,3	2,0	2	0
chamber	12	0,7	0,9	2	0
Tar fraction, °C					
230—320	31	0,6	0,9	2	0
320—360	47	1,0	2,0	2	0

Note. On plates of steel 10 in accordance with GOST 9.054-75.

tial evaporation and oxidation temperatures are characteristic for these substances. Shale tar and its fractions contain a large amount of oxygen compounds - surfactants that have inhibiting action. The protective properties of shale tar and its distillation products were evaluated by the methods of GOST [All-Union State Standard] 9.054-75 on plates of steel 10 and copper M1. For comparison petroleum-based commercial slushing oil K-17 and oil prepared with corrosion inhibitor AKOR-1 were tested.

The results (Table 2) indicate that the gas generator tar exhibits better protective properties than the chamber tar. Consequently, the method of processing the oil shales has a significant effect on the protective properties of the resulting tar. With an elevation of the decomposition temperature of the shale the concentration of phenols in the tar decreases, the fraction of condensed aromatic hydrocarbons increases, and the character of the hydrocarbon and oxygen components changes [2]. Therefore, the composition of tars obtained by thermal decomposition of shale in chamber furnaces (at 700°C) and in gas generators (at 400-450°C) differs. It is not the amount of oxygen compounds, but rather their chemical character, that has a great effect on the protective properties of the tar. Thus, the chamber tar does not contain n-alkylketones, which are present in significant amounts in the gas generator tar and which evidently largely govern its protective properties.

An intensification of protective properties in corrosive gas-air media with an increase of the boiling point is characteristic for the 230-320 and 320-360°C fractions from atmospheric distillation of shale tar. This is in good agreement with the data of [2, 3]: with an increase of the boiling point of shale tar fractions the concentration of oxygen

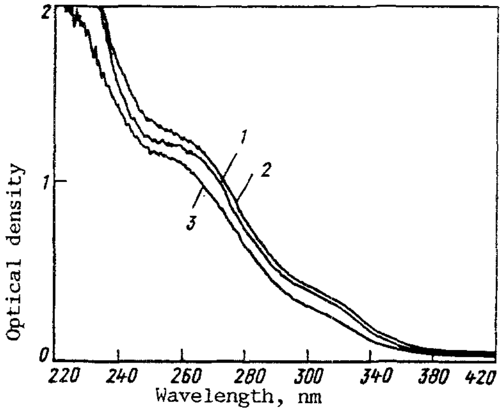

Fig. 1. UV spectra of 3% solutions of NaCl after tests of products from processing of shales (Specord M40 spectrophotometer, quartz cuvettes, ℓ = 1 cm): 1, 2) 230-320 and 320-360°C fractions of shale tar; 3) shale tar.

compounds in them increases, while the concentration of hydrocarbons decreases. The level of protective properties developed by gas generator tar and its high boiling distillates in a thin film is comparable with that for mineral oil containing 25% AKOR-1 corrosion inhibitor and less than for K-17 slushing oil.

The very high capacity of the shale tars and their high boiling fractions for effective displacement of a corrosive electrolyte (hydrobromic acid) from the surface of metal should also be noted. The oxygen compounds that are found in shale tar can be divided into neutral compounds (various ketones) and acid compounds (phenols) [3]. Therefore, it is the ketones and phenols that provide the high ability of the tars to displace the corrosive electrolyte from the surface of metal. A high displacing capacity is imparted to slushing materials of petroleum feedstock by adding inhibitors, which are organic acids, their salts and esters.

Another characteristic of shale tars and their fractions is poor protective properties in tests in sea water. The UV spectra of 3% solutions of the salts that form sea water (NaCl, $CaCl_2$, $MgCl_2$, Na_2SO_4), after gas generator tar and high boiling fractions of tar mixtures have been tested in them (see Fig. 1), correspond to the spectra of aromatic compounds containing a hydroxyl and a conjugated carbonyl group, i.e., phenols (λ = 270 nm) and aromatic ketones (λ = 300-350 nm). Therefore, a part of the oxygen compounds is soluble in aqueous solutions of salts of sodium, calcium, and magnesium.

The chemical behavior of aromatic compounds that contain hydroxyl and carbonyl groups can be attributed to significant polarity, which determines the high reactivity of phenols and ketones. Phenols, which differ in their properties from the other components of shale tar, because of their acid function and capacity of their salts (phenolates) to dissolve in water, are washed away in the sea water tests, thereby reducing the protective efficiency of the tar. Ketones, because of the presence of the C=O polar group, are partially soluble in sea water, including those due to complexing with metal cations, which also causes a reduction of the protection effectiveness of the tested products in sea water. In tests on copper plates (Table 3) shale tar and its distillation products are superior to K-17 oil with regard to protective effectiveness, and at high temperatures they are less corrosive.

The results of these tests allowed us to develop the slushing oil Slaks,* which is based on the high-boiling fraction of shale tar and a corrosion inhibitor of petroleum origin that contains nitro compounds. This oil gave positive results in field tests on agricultural equipment. It is capable of protecting equipment without additional protective [sealing] agents for a period of 6-8 months in open areas and 2-3 years under sheds. Predictions of the protective effectiveness of Slaks oil by the qualifications technique of [4] based on laboratory tests allowed us to determine guarantee periods of protection of equipment against corrosion under average and mild conditions: respectively 7 and 10 years. Because of its high displacing and penetrating capacity, it can be used for protection of wet and poorly prepared surfaces. Industrial production of Slaks slushing oil has been set up at the Slantsekhim Production Organization (city of Kokhtla-Yarve).

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*GOSNITI colleagues A. É. Severnyi, E. A. Puchin, and V. G. Bryukhanov participated in this work.

TABLE 3

Sample	Protective properties (in accordance with GOST 9.054-75 in plates of M1 copper)		Corrosivity (in accordance with GOST 2917-76), points
	sulfur dioxide chamber: weight loss (in five cycles), g/m^2	immersion in sea water: degree of damage (10 days), %	
Shale tar			
gas generator	0,7	0	1a
from chamber furnaces	1,4	30	1a
Tar fraction			
230—320 °C	2,3	50	1a
320—360 °C	0,3	30	1a
K-17 slushing oil	3,9	70	3a

TABLE 4

Product	First signs of corrosion, cycles			Surface damage (HBr displacement, 4 h), %
	sulfur dioxide chamber	immersion in sea water	hydrochloric acid mist	
Compound				
MSA	>15	>50	25	40
BLK	8	>30	6	15
Kukersol varnish	4	>30	6	20
Movil	6	>60	14	0
NG-216B	10	>50	10	0
NG-222A	22	90	30	0

Note. On plates of steel 10 in accordance with GOST 9.054-75.

Thus, we have established the very good protective properties of shale tar and its distillates, their capacity for effective displacement of corrosive electrolytes from the surface of metal, and the absence of corrosivity with respect to nonferrous metals at high temperatures. Taking into account the low pour point, the high initial oxidation temperature, the viscosity properties and relatively low cost, it will be expedient to use shale tar and its high boiling fractions as components of combination corrosion inhibitors, plasticizers for film-forming inhibited petroleum compositions (PINS) and especially as bases for slushing oils.

The protective properties of a number of commercial products of the shale processing industry - Kukersol varnish, MSA and BLK compounds - were investigated in order to study the possibility of using the products of oil shale refining in the production of slushing materials. Kukersol varnish is produced in significant quantities and is used both independently as a corrosion-protective coating and as a component of roofing compounds. It is produced by the condensation of shale tar with formalin in the presence of an alkali catalyst and by dissolving the resulting product in light hydrocarbons. BLK roofing compound is obtained by mixing Kukersol with bitumen, latex, and if necessary with mineral fillers (cement, asbestos). MSA automative compound is intended for protection of the bottoms of automobiles.

Dense and stable protective films form after evaporation of the solvent when these products are applied to a metal surface. With regard to composition and character of the film that forms Kukersol, BLK, and MSA resemble PINS. Therefore, their protective effectiveness was evaluated by comparing it with known commercial PINS - Movil, NG-216B, and NG-222A. The results (Table 4) indicate that the products of shale refining have good protective properties, ones that are comparable, and in a number of cases superior, to the commercial products. They are slightly inferior to PINS with regard to their ability to displace a corrosive electrolyte from the surface of metal. In addition, with time, films of them on a metal surface polymerize and harden under the effect of external factors.

As a result the protective ability of the film improves, but it becomes significantly more difficult to remove the coating. After the tests, films of Kukersol, BLK, and MSA could be removed only with acetone, with traditional solvents (gasoline and white spirits) being ineffective. These problems limit the independent use of these products as agents for temporary corrosion protection. Nevertheless, many of the components of Kukersol varnish and BLK and MSA compounds can be used in developing new film-forming compositions that optimally combine the products of shale and petroleum origin.

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