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RADIOISOTOPES IN THE INVESTIGATION OF LUBRICANT PROPERTIES

by

Yu. S. Zaslavskiy and G. I. Shor

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By: Yu. S. Zaslavskiy and G. I. Shor

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ABSTRACT

The optimum compostion of neutralizing additives of motor oils is determined by studying the mechanism of their action under conditions of modeling during which the appropriate functional property of oils with additives most clearly appears. Studies were made on the RVM-1 (radioactive tracer apparatus for testing oils), modeling conditions which determine the process of corrosional wear of the cylinder-piston group of internal combustion engines. A diagram of this apparatus is given in Fig. 1. The remaining part of Chapter 1, deals with the influence of the chemical composition of additives on the effectiveness of neutralizing action of additives. Chapter 2, discusses the investigation of counterwear properties of additives to oils in conditions of electroerosional wear, and Chapter 3, deals with the study of the mechanism of detergent action of additives to motor oils. In Chapter 4, the investigation of the mechanism of anticorrosive action of additives to oils is discussed, and Chapter 5, deals with the investigation of the mechanism of action of countersizing additives. Also discussed here is the mechanism of action of molybdenum-organic additives to oils. In Chapter 6, certain peculiarities of wear of internal combustion engines with the application of oils with additives are discussed, and the last chapter covers the investigation of the influence of different additives on counterwear properties of liquids for hydraulic systems. [illegible]
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INTRODUCTION

Radioactive isotopes have found wide application in the investigation of friction, wear, and properties of lubricants [1-6] after the patent of Ferris [7] and work of Clark, Gallo, and Lincoln [8] were published in 1943. Ferris proposed the introduction of phosphorus-32 (obtained on a cyclotron) into cast iron, from which piston rings of an internal combustion engine were made. Wear of the piston ring was recorded by measuring radiation of the isotope of phosphorus-32, which was accumulated together with products of wear in oil circulating in the engine.

Pinotti and coauthors [12], for the investigation of wear of a one-cylinder engine, used a piston ring irradiated by neutrons in the channel of a nuclear reactor. Such a method of obtaining radioactive components in the investigation of friction, wear, and the study of properties of lubricants possessed many advantages as compared to the method proposed by Ferris and therefore obtained very wide application in many countries [2, 4-6].

Lancaster [5] especially stresses that rapid propagation of the method of tracers for investigations of the mechanism of processes of friction, wear, and lubrication is connected with the fact that it is possible to observe the highly complex effects which are developed with the slip of surfaces of friction — the transfer of metal and formation of products of wear during the deformation of surfaces.

Clark and coauthors [8] used for the first time sulfur-35 with synthesis of additives to lubricating oils for study of the process of formation by additives of films on surfaces of metals.

Today when there has been accumulated already more than twenty years of experience in the application of radioactive isotopes in the investigation of properties of lubricants, it is possible to affirm that in an overwhelming majority of published works with the help of radioactive isotopes there is studied basically the ability of lubricating oils and additives to decrease the wear of machine parts and mechanisms. With this, as a rule, radioactive isotopes are used for improvement of the method of wear tests and for their acceleration [9-15], i.e., basically for comparative tests and not as a very effective means of scientific investigations.

Best results are achieved by radioactive isotopes in scientific investigations when using them in combination with other methods. Such a combination permitted obtaining very interesting experimental data, in particular, during the study of properties of lubricants and especially during the study of the mechanism of action of additives to oils. The authors raised the problem to show this both in data of their investigations and in terms of works published in literature.

It should be noted that the scientific community of the United States, England and the other most technically well-developed countries highly evaluates the contribution of the Soviet Union in the field of study of the mechanism of the action of additives to oils with the help of radioactive isotopes, which founds its reflection in surveys made in the United States by Godfrey and in England by Lancaster.

CHAPTER 1

INVESTIGATION OF THE MECHANISM OF NEUTRALIZING ACTION OF ADDITIVES TO OILS

Radioactive Tracer Apparatus RUM-1

Of the three forms of wear of the cylinder-piston group of internal combustion engines – abrasive, erosional and corrosional [16] – the last one usually plays the biggest role, especially with the use of fuels with increased sulfur content [17]. Wide comprehensive investigations, conducted in many countries during the last 30 years, showed that corrosional wear of cylinders of an engine is connected with the formation (during combustion of fuel) of acids (sulfuric, sulfurous, carbonic, nitric, and low-molecular organic acids – formic, acetic, and others), anhydrides of acids and other corrosive compounds. According to data published by McConnell and Nathan [18], during the combustion of diesel fuels with increased sulfur content in a composition of acids forming in cylinders of a diesel engine, there is contained up to 80% of sulfuric acid.

In many works it is shown that electrochemical and gas corrosion of walls of cylinders and piston rings can occur. Electrochemical acid corrosion causes the most intense wear, and the formation of acids can be observed not only at low but also at high operating temperatures due to the increase in due point at high-pressures in cylinders and the presence of an anhydride of sulfuric acid [18-20]. Thus, according to data of B. B. Genbom [19], coinciding with data of Van der Zijden and Kelly [20], condensation of steam from products of combustion in an engine occurs at temperatures of walls of the cylinders of 110-135°C for diesel engines and 135-165°C for carburetor engines.

Conducted recently by McConnell and Nathan [18], thorough investigations of the mechanism of wear of the cylinder-piston group of diesel engines operating on heavy residual fuels with a different content of sulfur showed that abrasive wear with the application of sulfurous fuels is a direct result of corrosional wear: products of corrosion, iron sulfates, under conditions of high temperatures in cylinders of a diesel engine are turned into oxides possessing abrasive properties. The possibility of such transformation is proven by the specially set laboratory experiments.

Proceeding from the conventional concept on acid corrosion as the basic determining cause of wear of the cylinder-piston group of internal combustion engines, during the last 20 years there have been widely developed works on the synthesis, test and production of alkali additives to oils allowing effectively to reduce corrosional wear as a result of neutralization of the acids.

Intense development of such works is also connected with the fact that Dyson, Richards, Williams [21], Blanchier and Raine [22] and other authors advanced the affirmation on the presence of the direct connection between ability of alkali additives to neutralize corrosional wear and the absence of deposits on parts of an engine with the application of ucn additives [18, 21-23, 25]. The indicated connection, in the opinion of these authors, is based on the fact that the acids forming during combustion of fuel and oxidation of oil not only cause corrosional wear but also are initial products with the formation of resinous substances and lacquers serving as binding agents for carbonaceous particles and entering together with them into a composition of deposits on parts of the engine. All of this led individual researchers [22, 23, 26, 27] to the point of view on the existence of a certain minimum necessary level of alkalinity of oil with the neutralizing additive. This level provides minimum wear and cleanness of the parts during operation of the engine independently of the chemical composition of the alkaline additive.

Such a point of view was refuted by Tourret and Bale [24] and later by Ponderoyan and coauthors [28, 29], who with the help of engine tests showed that with equal alkalinity different additives provided unequal effectiveness of the lowering of corrosional wear and various effectiveness of detergent action.

Recently J. Wakuri and others [30] showed that oil with a neutralizing additive during breaking-in can cause increased wear of piston rings of a ship diesel engine.

However, during these investigations conducted on engines there is not established the mechanism of action of tested alkali additives. In particular, it is not determined how the chemical composition of additives influences the effectiveness of the neutralizing action. Obviously, it is possible to determine the optimum composition of neutralizing additives to motor oils not according to data of tests in engines but only by studying in detail the mechanism of their action under conditions of modeling at which the appropriate functional property of oils with additives appears most clearly.

Investigations were conducted on the apparatus developed by us [31-33],[RUM-1] (РУМ-1) (radioactive tracer apparatus for testing oils), having modeled conditions which determine the flow of process of corrosional wear of the cylinder-piston group of internal combustion engines. A diagram of the apparatus is shown in Fig. 1.

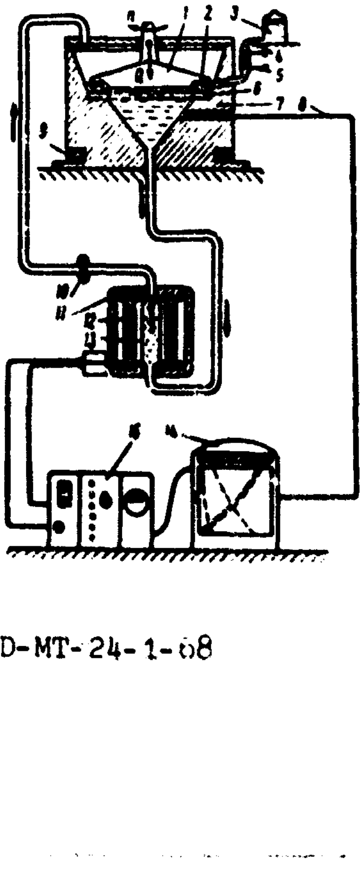

Fig. 1. Diagram of the radioactive tracer apparatus RUM-1 for the determining of neutralizing effectiveness of additives to motor oils: 1, 2, 6, 7 - friction machine with radioactive side blocks; 3, 4, 5 - supply system of vapors of solutions of corrosive acids to the rubbing surfaces; 8 - thermocouple; 9 - electroheating; 10 - pump; 11, 12, 13 - lead chamber with Geiger counters for measurement of radioactivity of the circulating oil; 14 - recording electronic potentiometer; 15 - radiometric apparatus.

As can be seen from the diagram, in the oil main line of the apparatus RUM-1 there is included a measuring reservoir 13 surrounded by a unit of six gamma-ray counters 12 in a lead chamber 11. The intensity of γ-radiation recorded by the counters is registered by the radiometric apparatus 15 and electronic potentiometer 14.

As can be seen from Fig. 1, the unit of friction of the apparatus RUM-1 constitutes a cast-iron ring 6 against the upper face of which is carried out friction of two cast-iron side blocks 2 activated by isotope Co^{60} by pressing of the cylindrical inserts with a diameter of 0.9 and height 1.5 mm. During operation of the apparatus RUM-1 friction surfaces of the pad and ring wear out, and products of wear, including atoms of the radioactive isotope Co^{60} enter the oil. The circulation of the oil, carried out with the help of gear pump 10, through a measuring reservoir with a unit of counters permits continuously recording the accretion of radioactivity of the oil in connection with the accumulation of radioactive metal in it.

An aqueous solution of acid (for example, acetic, formic, or sulfuric) with an acid number of 8 mg KOH[1] is filled in a bottle from which through a capillary tube it enters by drops into the evaporator from quartz glass where it completely evaporates. Formed in evaporator at a temperature of 400°C, superheated steam through a nozzle proceeds by jets to rubbing surfaces. The supply speed of acid in the evaporator is 25 drops per minute.

Into the bath of the RUM-1 are filled 350 cm^3 of oil. The apparatus operates at 720 r/min and a specific load of 8 kg/cm^2, and the temperature of oil is 50°C. Vapors of acid do not move until there approaches a constancy of rate of wear, which is easily determined visually from the graph recorded by the potentiometer after which there is included a supply of acid vapors.

Figures 3 and 4, for example, give characteristic curves of the wear of rubbing surfaces recorded automatically in the process of investigations on the apparatus RUM-1.

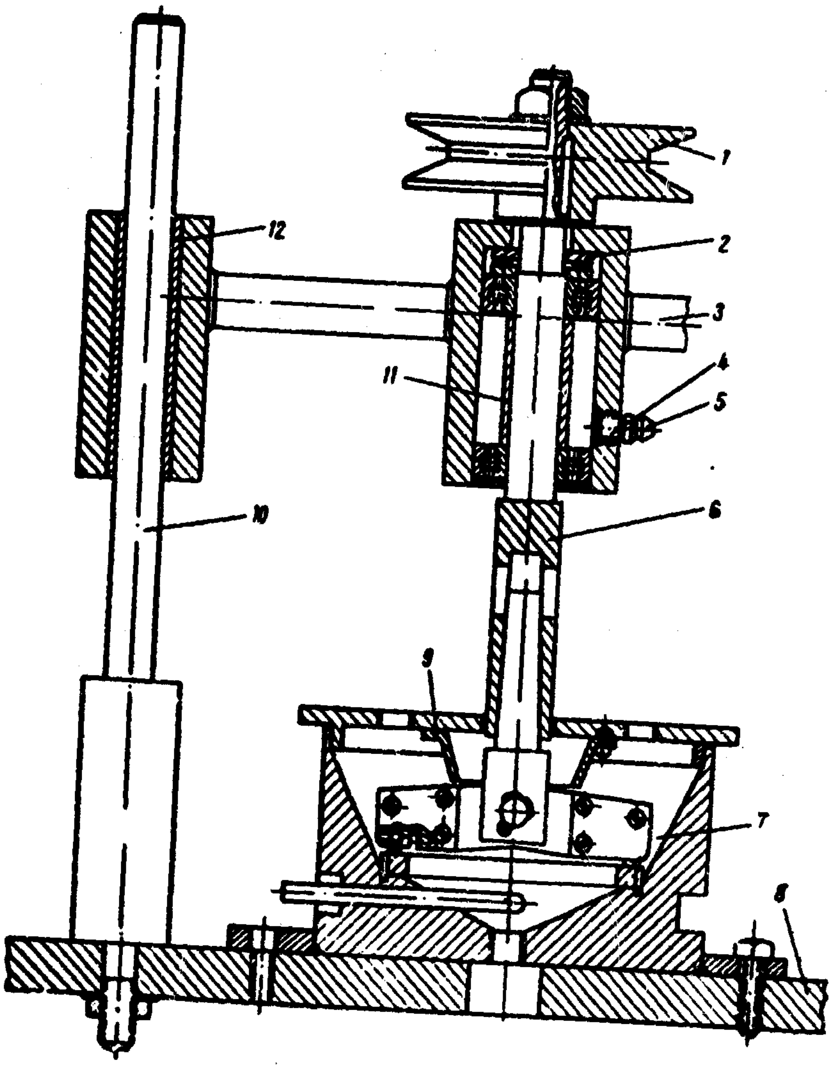

Fig. 2. Friction unit of the apparatus RUM-1: 1 - pulley; 2 - thrust bearing; 3 - loading central subassembly; 4 - radial bearing; 5 - lubricator; 6 - shaft; 7 - friction machine; 8 - adjusting plate; 9 - oil deflector; 10 - directing stand; 11 - thrust bushing; 12 - load bushing.

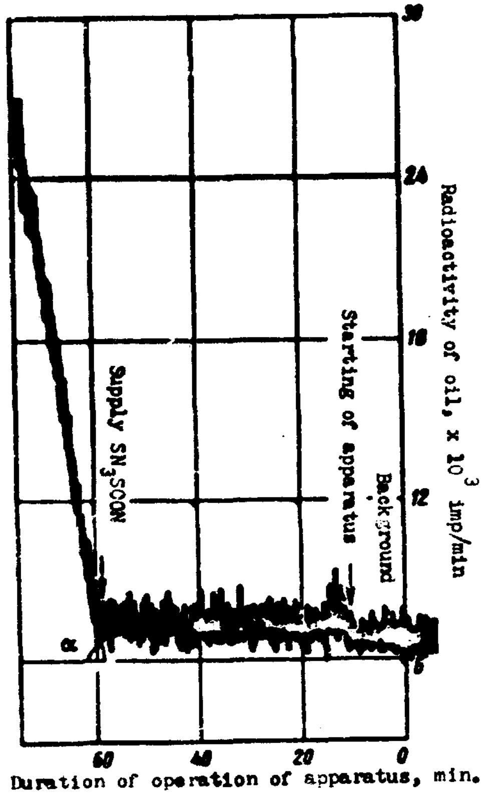

Fig. 3. Automatically recorded diagram of wear during a test of motor oil without an additive on the apparatus RUM-1. [CH_3COOH = = SN_3SOON]

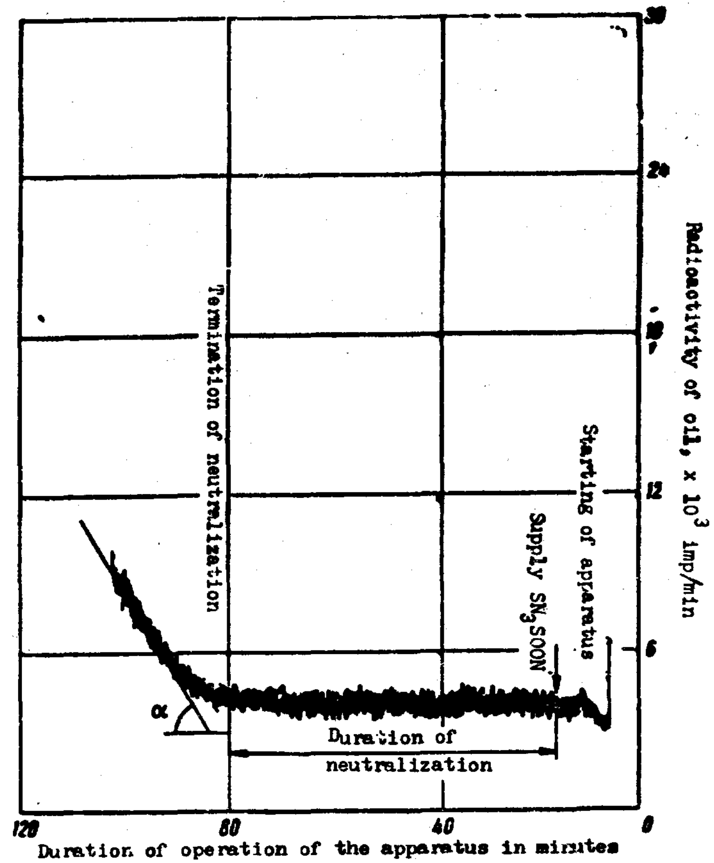

Fig. 4. Automatically recorded diagram of wear during a test of motor oil with neutralizing additive on the RUM-1 apparatus.

Influence of Chemical Composition of Additives on the Effectiveness of Neutralizing Action

Modeling of conditions of operation of the cylinder-piston group of engine on the laboratory apparatus RUM-1 permitted investigating the influence of chemical composition of additives to motor oils on the effectiveness of their neutralizing action [34].

Investigations were conducted with a supply of vapors of acetic and sulfuric acids to rubbing surfaces working with motor oils [AS-5] (AC-5) and AS-9.5 (from sulfurous oils) with 3% disulfide alkylphenolate of sodium, calcium, barium, lithium and potassium. In the process of the experiments there were determined the duration of effective neutralization of corrosional wear and the rate of wear of rubbing surfaces upon completion of neutralization. After the experiment acid numbers of the oil and condensate were determined, and radioactivity of the oil and condensate were measured. After every experiment on oil with an additive the rubbing surfaces were brought to an identical initial state, conducting experiment on oil without an additive with a vapor supply of the same acid. Results of experiments on oil AS-9.5 with additives with a vapor supply of acetic acid are given in Table 1.

Since salts of corrosive acids are badly soluble in mineral oils but are soluble in water, the presence of radioactivity in the condensate should be interpreted as an indicator of corrosional wear. The appearance of radioactivity in oil, just as the lowering of acidity of the condensate (initial acidity 8 mg KOH) and growth of acidity of oil (initial acidity of oil without additive – 0.04 mg KOH, and the initial oil with additives gave an alkali reaction), is evidence of the neutralizing action of the additives.

Considering what has been said, it is possible to affirm that additives with different cations provided effective lowering of corrosional wear as a result of the neutralizing action.

The quantity of sulfur contained in all the tested additives was identical, and therefore the anticorrosive action due to the

Table 1. Influence of cation and quantity of neutralizing additive on the corrosional wear of rubbing surfaces.

Test product	Duration of effective neutralization, min	Rate of wear, (imp/min)/h	Radioactivity after experiment,* imp/min		Acid number after experiment, mg/KOH		Normal electrode potential of cation of additive, V	Solubility of acetate of salt, g/100 g H_2O
			oil	condensate	oil	condensate		
Oil AS-9.5 without additive ..	0	18,000	0	9,026	0.06	6.0	-	-
Oil AS-9.5 with additive:								
Disulfide alkyphenolate, 3%:								
potassium	50	6,000	136	12,680	0.27	Alkali medium	-2.92	129.5
lithium	50	6,600	104	3,644	0.34		-3.01	68.6
barium	50	7,050	206	9,433	0.22	"	-2.92	37.8
calcium	50	7,350	48	9,382	0.15	"	-2.84	75.8
sodium	50	7,800	272	4,768	0.41	"	-2.71	65.3
the same, 1.5%	20	8,700	50	13,925	0.14	"	-2.71	65.3
" 6%	80	5,200	416	3,584	0.53	"	-2.71	65.3
" 9%	120	4,900	696	2,448	0.66	"	-2.71	65.3

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*Numerical data given in this column only qualitatively characterize the process.

formation of protective films by these additives was in all cases identical and did not have an effect on the influence of cations.

The correspondence between rates of wear and the position of cations (see Table 1) of additives in electromotive series (an exception is potassium, the acetate of which has an abnormally high solubility in water) shows that as a basis of the mechanism of

Table 2. Influence of solubility of sulfates on wear of rubbing surfaces.

Additive	Rate of wear (imp/min)/h during work with			Solubility of sulfate of layers, g/100 g H_2O	Normal electrode potential cation of additive, V
	transformer oil	oil AS-5	oil AS-9.5		
Disulfide alkylphenolate:					
sodium	1050	400	875	32	-2.71
lithium	1600	330	365	24	-3.01
calcium	2175	1100	1400	0.2	-2.84
barium	3000	1050	1400	0	-2.92

anticorrosive action of neutralizing additives lie the electrochemical processes. The most effective additives should contain cations with the greatest negative normal electrode potential and form during neutralization of corrosive acids of salt, which are very soluble in water and therefore do not have an abrasive action on the rubbing surfaces. The most evident influence of solubility of the indicated salts can be seen from results of experiments conducted on various oils with additives with vapor supply of sulfuric acid (Table 2).

A peculiarity of the process of wear during work of the neutralizing additive, as can be seen from Fig. 4, is the change in rate of wear in the process of the vapor supply of acid. Apparently, at first there occurs effective neutralization of the supplied acid by additive in a volume of oil with simultaneous transition of cations of additive in the accumulated condensate. The point of the bend of the wear curve corresponds, obviously, to the complete transition of metal of the additive in the condensate. The more the additive is contained in the oil, the greater the time required for transition of cations into a condensate, the longer the provision of effective neutralization and the less the rate of corrosional wear after full transition of cations of the additive into a condensate (see Table 1). Everything that has been said is confirmed by a checked change in the ash content of oil with additive in the process of the experiment, showing a sharp decrease in the content of cation of the additive in oil after the bend of the curve (see Fig. 4). In experiments with vapor supply of sulfuric acid the neutralizing action of the additives appeared somewhat less clear than with a supply of acetic acid, but there was observed greater deceleration of the wear. This is connected with the effect of the interaction of sulfuric acid with components of oils with the formation of sulfonic acids providing additional protection of the rubbing surfaces. The latter is shown by specially conducted experiments with the introduction into oil of 0.1% sulfonic acids. In these experiments with supply to rubbing surfaces of vapors of acetic acid, corrosional wear was retarded due to the formation of protective film on metal by introduced sulfonic acids.

Checked also was the influence of anions of neutralizing additives on the effectiveness of anticorrosive action of the latter. Experiments were conducted with a vapor supply of acetic acid to rubbing surfaces operating on oil AS-9.5 with different substances containing calcium introduced in such quantities in order to provide an identical content of calcium in the oil (0.15%). The following were tested: alkylphenolate additive [TsIATIM-339] (ЦИАТИМ-339) [Editor's NOTE: TsIATIM = Central Scientific Research Institute of Aviation Fuels and Lubricants] with cation of calcium, additive [MNI-22k] (МНИ-22) [Editor's NOTE: MNI = Moscow Petroleum Institute] (dialkyldithio phosphate of calcium), and also products containing calcium sulfonate - oil [PSK-1] (ПСК-1) and oil Rimula-Oil-30, introduced into oil AS-9.5. Results of these experiments are given in Table 3.

From Table 3 it is clear that the additive TsIATIM-339 (calcium) and MNI-22k with identical calcium content provided considerably greater anticorrosive effect than that of PSK-1 and Rimula-Oil-30. From this table it follows that in contrast to the other three products, as is evident from data of the change in ash content of oil, for alkylphenolate additive cations practically completely turned into condensate, and then the most prolonged effective neutralization with

Table 3. Influence of anions of neutralizing additives on corrosional wear of rubbing surfaces.

Test product	Duration of effective neutralization, min	Duration of experiment up to identical magnitude of wear, min	Rate of wear (imp/min)/h		Ash content of oil, %	
			during effective neutralization	after termination of effective neutralization	before experiment	after experiment
AS-9.5 + TsIATIM-339 (calcium)	130	175	100	6800	0.44	0.02
AS-9.5 + MNI-22k	60	120	150	4000	0.55	0.09
AS-9.5 + PSK-1	30	50	1500	8000	0.60	0.23
AS-9.5 + Rimula Oil-30 . .	60	65	1200	8000	0.53	0.26

the least rate of wear was observed. It seems to us that the most effective anticorrosional action of the calcium additive TsIATIM-339 is determined by the fact that the calcium in it is connected unstably and is easily detached even under the influence of very slightly acid media, whereas in remaining additives of the bound of calcium in different molecules are unequal and according even under the influence of acetic acid the splitting of calcium occurs only partially. With this, probably, is connected a less effective anticorrosive action of such additives if they are introduced into oil in small quantities.

It was checked whether there is an analogous effect with the use of oils with high additive content, having obtained propagation during the operation of diesel engines using high-sulfurous fuels. In Table 4 results are given of experiments using oil AS-9.5 with different additives containing equivalent quantities of metals in comparison with the oil Rimula-Oil-30 (0.6% calcium or 2.0% barium in the oil).

From Table 4 it is clear that in these investigations the

Table 4. Influence of high concentrations of sulfonate and alkylphenolate additives on the effectiveness of neutralization of corrosional wear of rubbing surfaces.

Sample of oil	Time of effective neutralization, min
AS-9.5 + calcium sulfonate neutral	40
Oil PSK-1	150
Oil AS-9.5 + PMSYa	320
Oil AS-9.5 + B-350	1260
Oil Rimula-Oil-30	240

alkylphenolate additive B-350 ([VNII NP-350] (ВНИИ НП-350)) [Editor's NOTE: VNII NP = All-Union Research Institute for Processing Petroleum and Gas and Production of Synthetic Liquid Fuel], in which the metal is bound the least stably, provided the most effective neutralization of corrosional wear. Of the three tested domestic sulfonate additives the most effective neutralization was provided by the "superalkali" additive [PMSYa] (ПМСЯ), which contains 3.5 times more calcium as compared to the stoichiometrical.

Results of these investigations confirm conclusions on the erroneousness of the viewpoint mentioned above that any neutralizing additive with sufficiently great content in oil will provide effective lowering of corrosional wear. It is quite obvious that the composition of the additive with an equivalent quantity of metal sharply affects the effectiveness of neutralization.

Thus, the conclusion can be made that the most effective neutralizing counterwear action will possess such additives whose cations can be easily detached under the action of acids. This requirement is satisfied by alkylphenolate additives. At the same time additives to motor oils should provide not only a neutralizing action but also a high detergent effect. A sharp increase in detergent effectiveness is attained with the mixing of alkylphenolate additives with sulfonate additives [35-37]. In connection with this there was checked the change in effectiveness of neutralization of corrosional wear with the use of mixtures with different relationships of barium alkylphenolate (VNII NP-350) and "superalkaline" calcium sulfonate (PMSYa): the total content of metals in all mixtures was identical and corresponded to 2% for oil (converted to barium). It was established that the effectiveness of linearly increased with an increase in the quantity of barium alkylphenolate in the mixture [34].

The expediency of the use of such two-component mixtures was indicated by Denison and Kavan [25]. They conducted studies on engines, and due to the simultaneous action of many factors having an effect on results of the test they could not clearly reveal the influence of each of the components on the effectiveness of neutralization and detergent action and also could not obtain clear data on the mechanism of action of the examined components. Moreover, Denison and Kavan did not determine the influence of two-component mixtures of various composition on the wear of engines.

Effect of Suppression of Neutralizing Action of Additives

In recent years as additives to motor oils there are being widely used different components of combination providing during the operation in the engine the corresponding functional action (neutralizing, detergent, anticorrosional, and so forth). However, in a number of cases it is established that with the mixing of components of additives there is observed impairment of their functional action [38-43]. Such a suppression of the functional action, for example, is established by Yu. S. Zaslavskiy with coauthors [40] with a comparison of neutralizing action of additives VNII NP-350, TsIATIM-339 and VNII NP-360 (Fig. 5). Figure 5 shows results of the determination of duration of neutralization of corrosional wear of radioactive friction of parts of the laboratory apparatus RUM-1 with the supply to it of vapors of a solution of corrosive acetic acid depending upon the concentration of barium in oil AS-9.5. One can see that the duration of neutralization linearly depends on the quantity of metal additives in oil.

Determination of the ash content of samples of oils after a test on the apparatus RUM-1 permitted establishing that during the

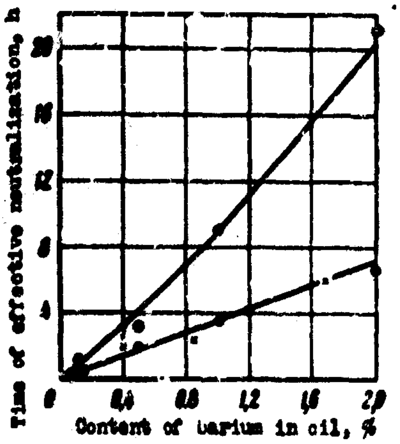

Fig. 5. Influence of concentration of different additives in oil AS-9.5 [NKZ] (HK3) on the duration of neutralization of corrosional wear. Tests were conducted on the laboratory apparatus RUM-1 with radioactive friction parts: o – additive VNII NP-350; × – additive VNII NP-360; ● – additive TsIATIM-339.

time of neutralizing of corrosional wear the barium, contained in all three additives, was completely expended. However, as one can see from Fig. 5, with identical initial concentrations of barium in the oil, the additive VNII NP-350 (barium alkylphenolate) provided a considerably greater duration of neutralization than that of the additive TsIATIM-339 (barium disulfide alkylphenolate) and VNII NP-360 (barium alkylphenolate in a mixture of zinc dialkydithiophosphate). Such a distinction in the neutralizing effectiveness of barium, contained in equal quantity in these additions, becomes intelligible if one were to assume that in the process of neutralization the barium in additives TsIATIM-339 and VNII NP-360 was expended not only in interaction with the corrosive acid, which was fed to the rubbing surfaces, but also with other components located in the composition of these additives (by sulfur or dithiophosphate component).

To check this assumption there was investigated a group of specially synthesized additives containing different sulfurous compounds with an unequal quantity of sulfur. These additives were introduced into oil AS-9.5 with such calculation that the quantity of barium in all cases would be identical. Experiments were conducted on the apparatus RUM-1 by the standard method with vapor supply of a solution of acetic acid. Results of experiments are given in Table 5 and in Figs. 6 and 7, on which there are shown dependences of the duration of effective neutralization and angle of inclination of the curve of wear of radioactive parts after termination of neutralization from composition and quantity of additives in oil expressed by the content of sulfur in the oil.

Table 5. Influence of chemical composition of additives on effectiveness of neutralizing action.

Additive	Content of additive in oil, %	Content in oil with additive, %		Duration of effective neutralization, min	Rate of wear after effective neutralization, (imp/min)/h
		barium	sulfur		
Barium alkylphenolate	5.0	0.55	-	180	1700
Barium alkylphenolate sulfurized by elementary sulfur	5.0	0.62	0.13	95	7200
Mixture of barium alkylphenolate (3 parts) with barium alkylphenolate sulfurized by elementary sulfur (2 parts) . .	5.0	0.57	0.05	120	4800
Barium sulfide alkylphenolate . .	10.2	0.55	0.37	150	2600
Barium disulfide alkylphenolate .	9.8	0.55	0.53	95	1100
Barium sulfide alkylphenolate fully replaced	5.3	0.55	0.18	160	1940
Barium disulfide alkylphenolate fully replaced	7.9	0.55	0.21	160	1050
Barium sulfide alkylphenolate of alkaline	3.75	0.55	0.11	-	1900
Mixture of barium alkylphenolate (5 parts) with sulphurized lubricating oil (1 part) . . .	6.0	0.55	0.025	155	1800
The same, 5 parts to 4 parts . .	9.0	0.55	0.1	40	2040
The same, 5 parts to 12 parts . .	17.0	0.55	0.3	20	3080
The same, 5 parts to 20 parts . .	25.0	0.55	0.5	18	2800

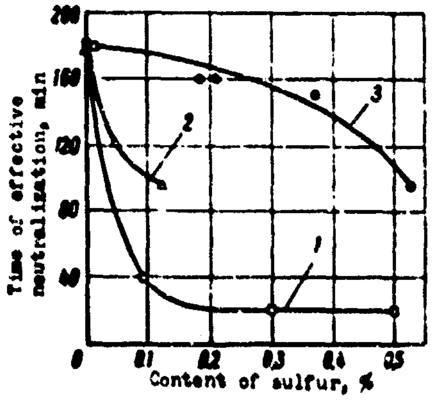

Fig. 6. Dependence of duration of neutralization of corrosional wear on the composition and quantity of additives in oil AS-9.5 expressed by the content of sulfur in oil: 1 - barium alkylphenolate in a mixture with sulphurized oil; 2 - barium alkylphenolate sulphurized by elementary sulfur; 3 - barium sulfide alkylphenolate; barium disulfide alkylphenolate.

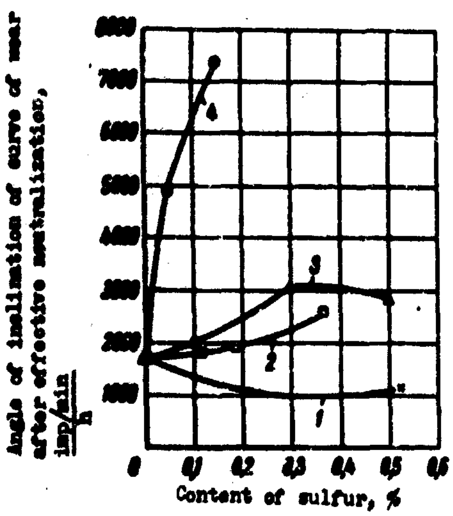

Fig. 7. Dependence of the angle of inclination of the curve of wear after termination of neutralization on the composition and quantity of additives in oil AS-9.5, expressed by the content of sulfur in oil:
1 – barium disulfide alkylphenolate;
2 – barium sulfide alkylphenolate;
3 – mixture barium alkylphenolate with sulphurized lubricating oil;
4 – barium alkylphenolate sulphurized by elementary sulfur;
mixture of barium alkypheolate with the same phenolate sulphurized by elementary sulfur.

As can be seen from Table 5 and Fig. 6, the effect of suppression of the neutralizing action of barium alkylphenolate depends on the content of sulfur in the additive: the more the sulfur in the additive, the less the duration of neutralization of corrosional wear. Furthermore, suppression of the neutralizing action depends also on the form of the chemical compound in which there is sulfur: the least suppression is observed during application of additives of barium sulfide alkylphenolate and barium disulfide alkylphenolate (curve 3); considerably more suppression during the application of barium alkylphenolate sulphurized by elementary sulfur (curve 2); the biggest suppression of neutralizing action occurred with a mixing of barium alkylphenolate with sulphurized oil (curve 1).

Such results are explained, obviously, by a different strength of the bonds of sulfur in molecules of the compounds, into the composition of which it enters. In particular, with sulfurization of barium alkylphenolate of elementary sulfur and with the mixing of it with sulphurized oil, the sulfur, apparently, is in such compounds which are easily able to detach it during destruction of the additive by acids. It is possible to assume that there will be formed also compounds which interact with barium ions, which lowers its consumption for neutralization of corrosive acids, i.e., leads to suppression of the neutralizing effectiveness and also to a high rate of wear after effective neutralization (curve 4 in Fig. 7).

However, greater suppression of neutralization with application of the last four additives in Table 5 (see Fig. 6, curve 1) is accompanied by lower rates of wear after effective neutralization (curve 3 in Fig. 7) than those in the preceding case. This is the result of formation by sulphurized oil of protective films on rubbing surfaces.

There is conducted a special experiment on the apparatus RUM-1 with nonradioactive rubbing parts and without a supply of acid vapors. The experiment was conducted with oil in which there was introduced as an additive 3% "sulphurized oil," labeled by the radioactive isotope S^{35}. After a 10-hour operation of the apparatus on oil with such an additive the side blocks of the apparatus are taken, washed and dried and the radioactivity on their rubbing surfaces is measured. The radioactivity proved to be equivalent to the presence on the surface of approximately 0.01 mg of sulfur/cm^2, which indicated the formation by the additive of a protective film on the rubbing surfaces of the side blocks. Further operation of the apparatus with these side blocks (with periodic measurement of radioactivity on their surfaces) on oil without an additive showed that full abrasion of the protective film is attained only after 25 h of operation of the apparatus. Thus it is shown that sulfur containing additives are able to form durable protective films on rubbing surfaces which lower corrosional wear.

The interaction between components leading to suppression of the neutralizing action is set also with mixing of barium alkylphenolate and basic calcium sulfonate [PMS-19] (ПМС-19) with dialkylide dithiophosphate components VNII NP-353 and 354 [40]. Results of the investigation of neutralizing properties of additives, mentioned above in Table 5, were compared with data 100-hour engine bench tests on the engine Д-35 given in Table 6. The engine operated on diesel fuel with a sulfur content of 1.0% and diesel summer oil. The tests were conducted in these conditions: n = 1420 r/min, fuel consumption, 7.3-7.4 kg/h, temperature of cooling water, 95°C, temperature of oil in crankcase, 90-95°C.

Table 6. Results of engine bench tests of oil with additives on the diesel engine Д-35.

Additive	Duration of neutralization, min (according to data of Table 5)	Content in oil with additive, %		Loss of weight of set of piston rings, g	Wear of engine, g iron/100 h	Content in carbon from first groove of piston, %	
		barium	sulfur			barium	iron
TsIATIM-339	95	0.5	0.4	0.78	1.13	12.8	0.29
TsIATIM-339p	160	0.5	0.2	0.40	0.96	16.9	0.23
VNII NP-350	180	0.5	0	0.35	0.83	19.3	0.19

[ЦИАТИМ-339п = TsIATIM-339p]

From Table 6 one can see that the least wear during operation of the engine on oils with the additive barium alkylphenolate is provided because of the most effective neutralization: the greatest content of barium and least content of iron in the carbon deposit indicate the greatest expenditure of barium on neutralization.

Comparative data on engine wear during operation of it on oil with additives of barium alkylphenolate (VNII NP-350), barium disulfide alkylphenolate (TsIATIM-339) and fully replaced barium disulfide alkylphenolate (TsIATIM-339p), completely coinciding with results of the determination of comparative neutralizing properties of oil with the same additives on the laboratory apparatus RUM-1, confirm the effect of suppression of the neutralizing action of barium alkylphenolate by sulfur contained in the additives.

An even more visual effect of suppression is seen in a comparison of results of engine bench tests with results of the determination of neutralizing action on the laboratory apparatus RUM-1 of not only fresh oil but also oil working in the engine. On engine Д-38 in the 100-hour method (n = 1420 r/min, fuel consumption, 7.5 kg/h, temperature of cooling water, 95°C, temperature of oil in crankcase, 90-95°C, diesel fuel with a 1% content of sulfur) there were tested

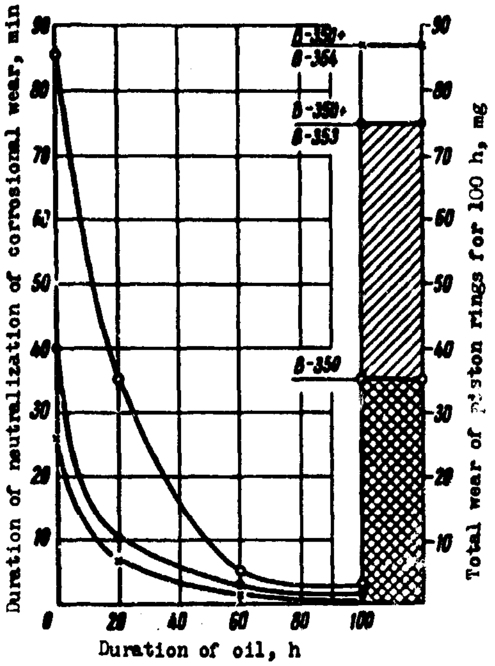

Fig. 8. Change in neutralizing effectiveness of DS-11 oil with additives depending upon the period of operation of oil in the diesel engine Д-38 (according to tests on the laboratory apparatus RUM-1). For a comparison the loss of weight of the set of piston rings is shown for 100 h of tests of a diesel engine using the same oils.

[DS-11] (ДС-11) oil with 2.86% additive VNII NP-350 and oil with the same additive in a mixture with dialkyldithiophosphate components: in one case, 1.11% VNII NP-353, and in another case – 1.14% VNII NP-354. After 20, 60, and 100 h of engine operation they removed the samples of oils whose neutralizing effectiveness was then determined on the apparatus RUM-1.

A comparison of results of engine tests with data of laboratory determinations is shown in Fig. 8. There is shown a loss in weight of the set of piston rings of the engine Д-38 during 100 h and a change in the neutralizing effectiveness of the oils in proportion to their work in engine. As can be seen from Fig. 8, the distinction in neutralizing effectiveness of the initial oils containing an equal quantity of barium, which was caused by the overwhelming action of the dialkyldithiophosphate components, is preserved during the entire period of operation of the oil in the engine, which determined the distinction in total wear of the set of piston rings during 100 h with operation of the engine on oil with these additives. At the same time results of these engine tests, given in Table 7, show that the increase in wear of the piston rings, connected with suppression of the neutralizing action of barium alkylphenolate by dialkyldithiophosphate components, is accompanied by a noticeable

Table 7. Results of engine bench tests of DS-11 oil with additives on the diesel engine Д-38.

Results of tests	Additives		
	2.86% B-350	2.86% B-350 +1.11% B-353	2.86% B-350+ +1.14% B-354
Quantity of carbon on the set of rings			
compression, g	0.109	0.132	0.092
deoiling, g	0.010	0.065	0.048
Quantity of carbon in grooves of the piston, g	0.930	0.373	0.317
Quantity of carbon on piston (except bottom), g	1.850	0.995	0.815
Wear of sets of piston rings			
compression, mg	30	65	72
deoiling, mg	5	10	15

decrease in the quantity of carbon, especially on pistons of the engine. Apparently, in certain cases it is necessary to use a mixture of components of additives which would possess satisfactory detergent action with small impairment of the neutralizing and, consequently, counterwear properties. However, it is more expedient to select such mixtures of components of additives in which there are no effects of suppression of some functional properties.

As can be seen from Fig. 8, during operation of oil in the engine, the concentration of active (i.e., able to be expended for neutralization of corrosional wear) neutralizing additive continuously descends due to the consumption in the reaction of neutralization. By adding fresh oil, carried out after 20 h for compensation of waste, the fall rate of concentration of the active additive lowers.

Results shown in Fig. 8 show that on the apparatus RUM-1 it is possible to determine the content of the active neutralizing component of additives in motor oils [44, 45].

Footnote

[1] The mentioned acidity was selected experimentally in order to obtain an identical acid number of the initial solution and condensate of vapors of acid during operation of the apparatus RUM-1 on oil without an additive.

CHAPTER 2

INVESTIGATION COUNTERWEAR PROPERTIES OF ADDITIVES TO OILS IN CONDITIONS OF ELECTROEROSIONAL WEAR

It was established by us that certain additives to motor oils are able to reduce electroerosional wear, which is observed in internal combustion engines along with the above-mentioned corrosional, erosional, and abrasive forms of wear. Electroerosional wear can occur due to the presence in an operating engine of electrical fields, which appear for different reasons, for example, because of the presence of a pair of metals (aluminum, steel, and others) in oil. The appearance of voltage between the aluminum piston and cast iron case of the cylinder, which are separated by a layer of oil, is experimentally established in works of Bodey [46] and Van der Horst [47].

To estimate the magnitude and direction of the electrical field which can appear between electrodes of different metals placed in oils of various chemical composition with different concentrations of additives, we conducted measurements with the help of a specially developed laboratory apparatus, since the carrying out of such measurements directly on the operating internal combustion engine is connected with great methodical difficulties.

Figure 9 gives a block diagram of the apparatus whose basic peculiarity of the measuring device is high sensitivity, obtainable owing to the application of a special d-c amplifier.[1]

The cell of measurement used in our investigations constitutes,

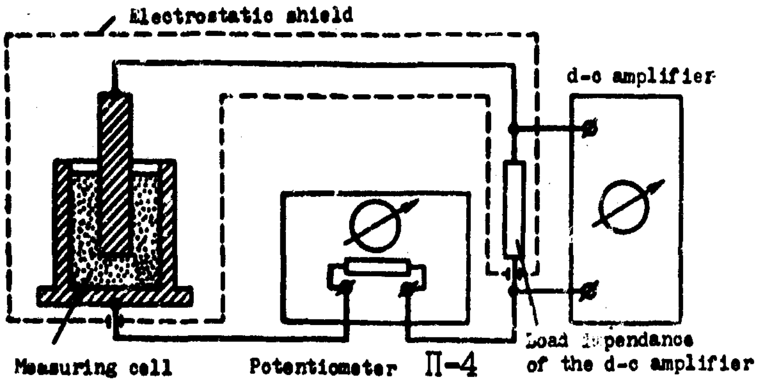

Fig. 9. Block diagram of experimental apparatus for determining the magnitude and direction of the electrical field which can appear between electrodes of different metals placed in oils of different chemical composition with different concentrations of additives.

as one can see from Fig. 9, a breaker of specific metal (in our case – duralumin) with a diameter (internal) of 14 mm and with walls 0.5 mm thick and 20 mm in height; into the shell are coaxially placed a cylindrical electrode with a diameter of 9 mm and height of 45 mm. Electrodes of different metals (duralumin, iron, lead, bronze, copper, tin) are set in the shell in such a manner so that the distance between the bottom of the shell and end of the electrode is 2.5 mm. The oil is filled near the installed central electrode, and the oil level is lower than the edge of the shell by 2.5 mm.

Measurements showed that the measured emf does not depend on dimensions of electrodes and the distance between them. Experiments were conducted where the central electrode was rotated at a speed of 60 r/min. These experiments showed that rotation of the electrode did not affect value of the measured emf.

The measurement cell (electrodes and oil between them) can be examined as a d-c generator possessing definite emf and internal resistance $r_я$. In order to measure the true value of emf, taking into account the voltage drop on resistance $r_я$, there is used a compensating measuring circuit in which the d-c amplifier serves as a zero-indicator. The source of the compensating voltage is the potentiometer П-4, on which the reading of the emf value is produced.

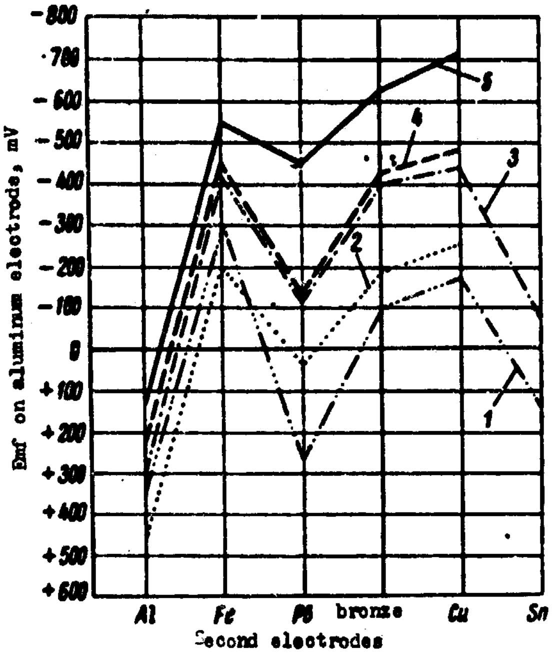

Fig. 10. Results of measurements of emf between electrodes of different metals separated by oil AS-6 with different additives: 1 – AS-6; 2 – 8.4% [PMS] (ПМС); 3 – 4.2% PMS + 13% B-370; 4 – 26% B-370; 5 – 18% Monto-702. The graph gives values of emf relative to the duralumin electrode.

Figure 10 gives results of measurements of emf with the use of a duralumin electrode in combination with electrodes from other metals; values of emf are given relative to the duralumin electrode.

From Fig. 10 it is clear that the magnitude of the emf depends not only on materials of electrodes but also on the chemical composition of oils and additives contained in them. Thus with the use of nonpolar naphthene-paraffin fraction of oil [AS-6] (AC-6) with any combinations of electrodes, the emf is not determined.

The measurements conducted showed that for certain combinations of metals and oils the magnitude of emf attains 1 V which coincides with data of the work mentioned above by Bodey [46]. Consequently, with clearances between parts of internal combustion engines there should appear an electrical field with an intensity of the order of several thousands of volts per centimeter. In the first place this pertains to continually changing clearance (during operation of the engine) between the groove of the piston and piston ring.

The electrical field should, apparently, cause increased wear of rubbing parts separated by a layer of lubricating oil similar to that which was observed under conditions of action of the electrical field with dry friction [48] or the cutting of metals [49].

Inasmuch as the investigation of electroerosional wear of parts directly in an internal combustion engine is conjugate with considerable methodical difficulties due to mutual influence of different forms of wear, we created a special experimental apparatus [RUM-2] (РУМ-2), which modeled the friction of the pair, cylinder-piston ring, with the application of d-c voltage between rubbing parts separated by a layer of lubricating oil.

Figure 11 gives a diagram of this apparatus. In the bath 9 of the friction machine there is set a cast iron ring 8 against the upper face of which there occurs friction of radioactive cast iron side blocks 7, which are mounted in the balance beam 6. The balance beam with the side blocks is rotated by an electric motor at a speed of 720 r/min. A load of 20 kg/cm^2 is created because of the weight of spindle 3 and guide bushings 4, freely sliding along tracks 5. Bath 9 is insolated from the working table, spindle 3, and balance beam 6 with the help of a spacer 12. To ring 8 and side blocks 7 (through sliding contact 2) is fed the d-c voltage 2 V from rectifier 11, and a negative potential is fed to the radioactive side blocks 7 whose wear is measured. With the help of pump 14 there is provided circulation of oil through the unit of Geiger counters 13, which permits continuously recording on the tape of the electronic potentiometer 16 radioactivity of the circulating oil (and thereby the wear of the side blocks 7) measured by the radiometric apparatus 15.

Figure 12 gives an automatically recorded diagram of wear during operation of the apparatus on motor oil [DS-11] (ДС-11) without an additive. From Fig. 12 one can see that there is observed a sharp increase in rate of wear with the application of d-c voltage between the rubbing parts.

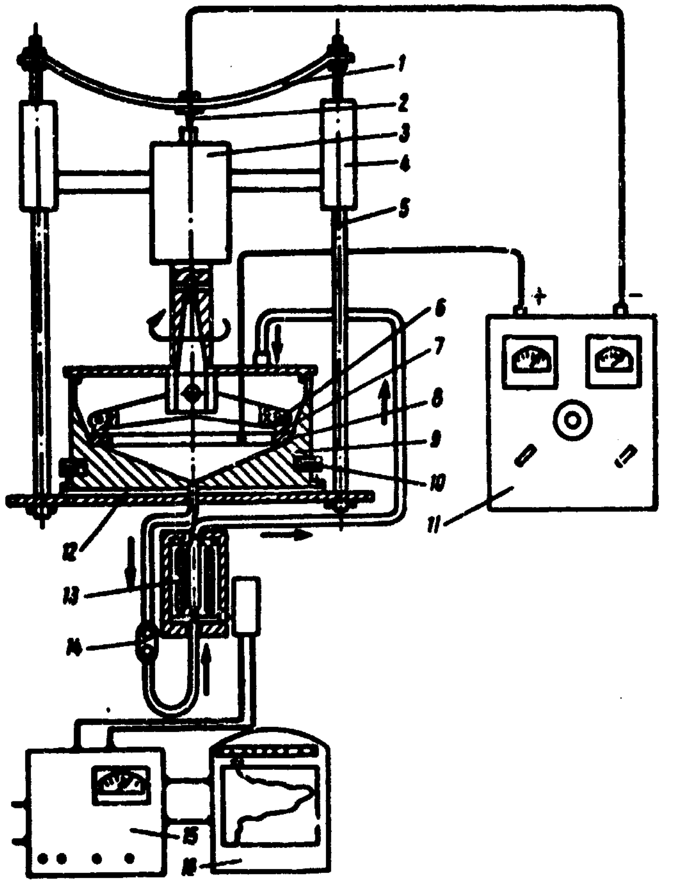

Fig. 11. Diagram of the experimental apparatus for investigation of counterwear properties of additives to oils under conditions of electroerosional wear: 1 – contact spring; 2 – sliding contact; 3 – spindle; 4 – guide bushings; 5 – directrixes; 6 – balance beam; 7 – radioactive cast iron pads; 8 – cast iron ring; 9 – bath; 10 – electroheating; 11 – rectifier; 12 – insulating layer; 13 – Geiger counters; 14 – gear pump; 15 – radiometric apparatus; 16 – electronic potentiometer.

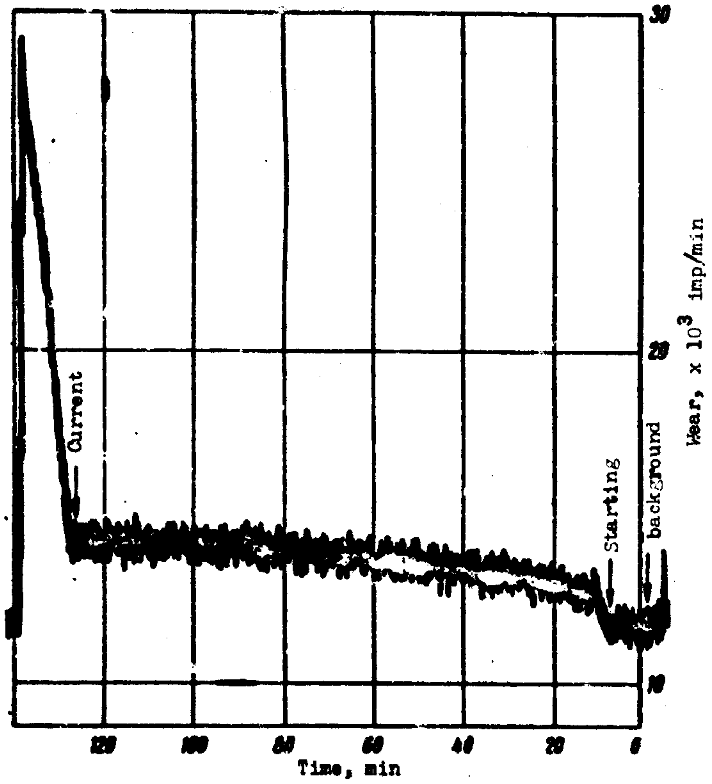

Fig. 12. Automatically recorded diagram of wear during operation of the apparatus on DS-11 motor oil without an additive. On diagram there are shown: a section of registration by radiometric instrumentation of the background of radioactivity ("background"); the moment of the beginning of operation of the experimental apparatus ("starting"); moment of beginning of the d-c voltage supply to the rubbing surfaces ("current").

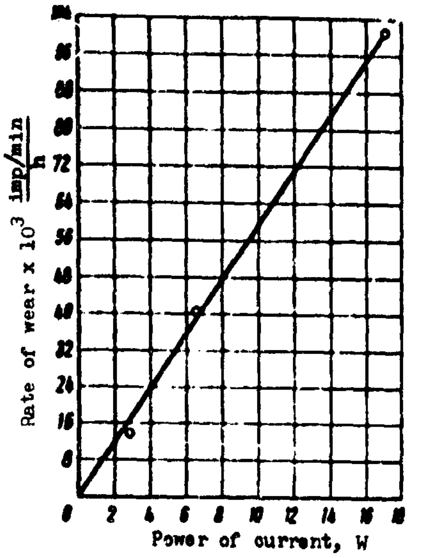

Fig. 13. Dependence of speed of electroerosional wear on power of passed electrical current.

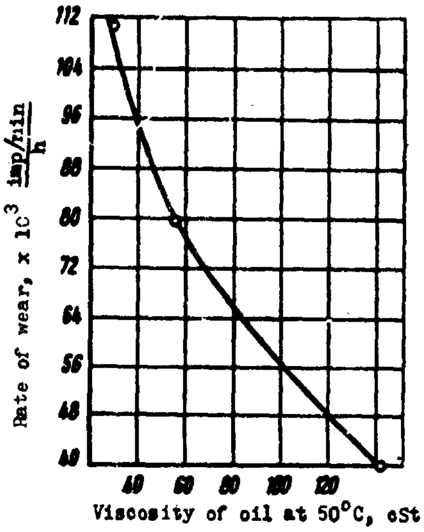

Fig. 14. Influence of viscosity of oils on rate of wear.

The influence of power of the passed electrical current on the rate of wear was checked. From Fig. 13 it is clear that the dependence of rate of wear on power of the current has a linear character. In the absence of a relative slip in rubbing surfaces even the peak power of current did not cause the appearance of radioactivity in the oil. Figure 14 shows that with a decrease in viscosity of oils the rate of wear is increased.

Thus given results of investigations confirm that during operation of the created apparatus, under conditions of d-c voltage feed to rubbing surfaces, there occurs electroerosional wear.

On the apparatus there were conducted investigations of counterwear properties of additives and compositions additives to motor oils. Figure 15 gives results of the investigation of DS-11 oil with additive (Fig. 15b), Orobis-267 (0.7%), and also results of the investigation of the same base oil before and after carrying out a test on an oil with additive. One can see very effective counterwear action of the additive: on the recorded diagram there is a section with decreasing rate of wear, connected, apparently, with the

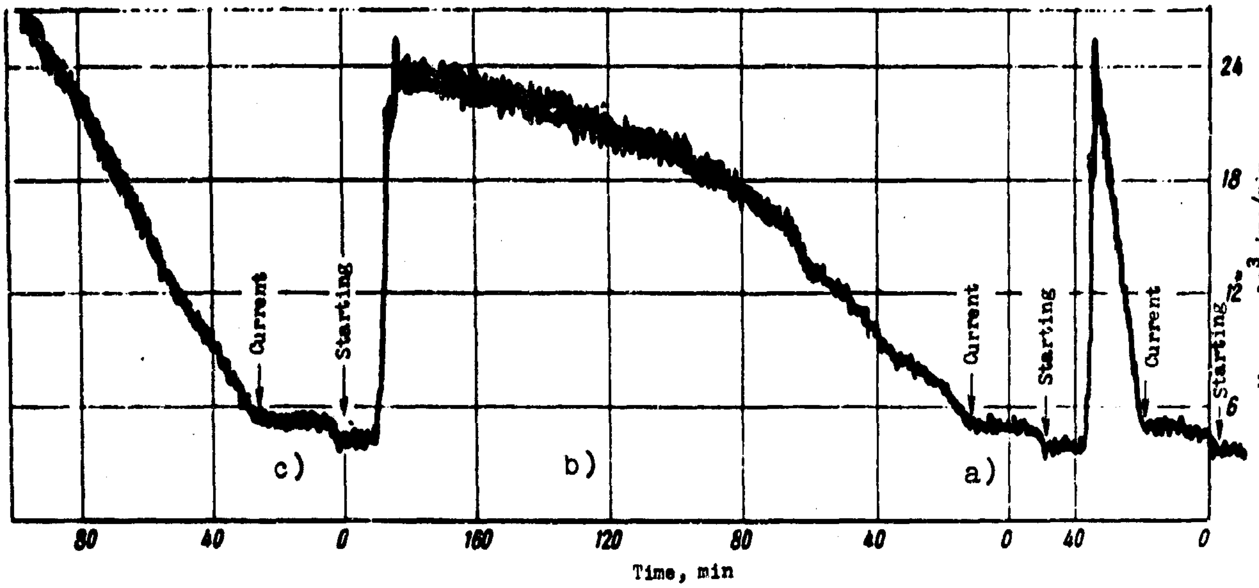

Fig. 15. Automatically recorded diagrams of wear during operation of the apparatus on motor oil DS-11 without additive (a) and (c) and with 7% additive Orobis-267 (b). On the diagram there are shown moments of the beginning of operation of the experimental apparatus ("starting"); moments of the beginning of d-c voltage of supply to rubbing surfaces of ("current").

formation by additive of counterwear film on rubbing surfaces, and a subsequent section reflecting the constant small value of the rate of wear. Formation by the additive of counterwear film on rubbing surfaces is confirmed by results of a test of oil without an additive (see Fig. 15c) after experiment on oil with an additive (see Fig. 15b): it is clear that the rate of wear on oil without an additive is considerably less than that on the same oil prior to a test of the additive (see Fig. 15a), which is explained by the preservation on the rubbing surfaces of a counterwear film formed by the additive during its test.

Thus the method developed permits characterizing not only the counterwear effectiveness of the additives in the process of their test but also the aftereffect of these additives, if there is one.

Proceeding from what has been said, we took the following method of estimatio of results of additive tests:

$$I = \frac{I_1 + I_2 + I_3}{3I_0},$$

where i is the index of counterwear properties of the additive; I_1 – initial rate of wear on oil with an additive, (imp/min)/h; I_2 – constant rate of wear on oil with an additive, (imp/min)/h; I_3 – speed of wear on oil without additive after experiment on oil with additive, (imp/min)/h; I_0 – speed of wear on oil without additive before the experiment on oil with additive, (imp/min)/h.

Table. Counterwear effectiveness of additives to motor oil DS-11.

Additive and its concentration in oil	Index of counterwear properties	Additive and its concentration in oil	Index of counterwear properties
DS-11 oil without additive	1.0	17% Orobis-2112a	0.27
1.0% Santolube-394 .	0.63	25% Orobis-218a .	0.15
0.7% Santolube-493 .	0.48	0.5% LZ-23k . . .	0.56
9% Monto-613	1.1	1.2% DF-11 . . .	0.40
9% Monto-613 + 0.7% Santolube-493 . . .	0.35	5% "A"	0.54
18% Monto-702	0.51	1.2% "Б"	0.19
0.7% Orobis-267 . . .	0.19	5% "A" + 1.2% "Б"	0.15
11% Orobis-2054 . . .	0.10		

[ЛЗ-23к = LZ-23k, ДФ-11 = DF-11]

Table 8 gives results of investigations of counterwear effectiveness of different additives to motor oil DS-11.

From Table 8 it is clear that the method developed permits not only estimating counterwear effectiveness of separate additives but also creating a composition of additives taking into account synergism with the combination of components. Thus the composition of additives 9% Monto-613 + 0.7% Santolube-493 and 5% "A" + 1.2% "Б" provide more effective counterwear action than that of each of the components.

Footnote

[1] A d-c amplifier constitutes two balance stages of amplification with resistance coupling. The first stage is built around a double electrometrical tetrode of the type [2E2P] (2Э2П) possessing grid

current of the order 10^{-14} A, which allows application in the grid circuit of high-megohm resistance. Currents appearing in the measuring cell have a magnitude of the order of 10^{-11}-10^{-13} A, and so that such a current creates a voltage drop sufficient to control the operation of the vacuum tube d-c amplifier, into the input circuit of the amplifier there are included resistances of the type [KLM] (КЛМ) with a face value of 10^{9}, 10^{10}, and 10^{11} Ω.

CHAPTER 3

INVESTIGATION OF THE MECHANISM OF DETERGENT ACTION OF ADDITIVES TO MOTOR OILS

Contemporary Concepts on the Detergent Action of Additives

The presence of electrical fields in internal combustion engines should have an influence not only on wear but also on the effectiveness of the detergent action of additives to motor oils. Detergent action, the ability to clean the parts of the engine, is one of the most important operational properties of motor oils.

With operation in the engine oil becomes intensively contaminated by highly dispersed particles of products of fuel combustion and oxidation of oil whose dimension does not exceed on the average 1 μm [50, 51]. Besides particles of such dimension in motor oil there are smaller particles. This permits examining the oil working in the engine as a colloidal system [52]. According to concepts well-developed in works of many authors [53] with respect to the mechanism carbon and lacquer formation, one part of the component of this colloidal system, resin and hydroxy acid, is in a molecular dispersed state, another part, asphaltenes, is in the form of bigger colloidal particles, and the third part constitutes hard insoluble particles of carbenes, carboids, and smoky products of incomplete combustion of organic substances on the surface of which surface active substances are adsorbed.

The hydrocarbon part of the oil on hot metallic surfaces of parts of the engine is oxidized up to the formation of lacquer film with simultaneous intense evaporation of light fractions of oil and low boiling products of oxidation.

The highly dispersed particles with resinous substances adsorbed on their surface under conditions of operation of the engine coagulate with the formation of enlarged conglomerates [52]. The resinous film constitutes a binding medium which holds on the metallic surface products of the change in oil and fuel with the formation of lacquer and carbon.

Thus the carbon formation and lacquer in the engine is determined by a whole complex of physical and chemical processes in which the important role is played by processes of the formation of products of oil aging and their interaction with hot metallic surfaces of parts of the engine.

Cleanness of engine parts can be provided with the help of additives to motor oils possessing different mechanisms of action. These additives either prevent or delay the accumulation of products of aging of the oil or provide a detergent action when the additive cleans the metallic parts of deposits and prevents formation of them, holding the insoluble products of oxidation and bodying of oil and fuel in a state of stable suspension.

The additive can delay accumulation in the oil of products of aging due to the increase in thermal and thermal oxidizing stability of the oil [54], the increase in its antioxidant properties, and neutralization of acid products forming in the oil in the process of exploitation [25]. The cleanness of parts of the engine can be increased as a result of pro-oxidizing action of additives when instead of sticky hydroxy acids and asphaltenes there will be formed compounds of the type of carbenes and carboids, which are fragile and easily washed from metallic surfaces [55, 56].

The detergent action of additives is a very complex process whose mechanism up to now has not been fully clarified. A considerable part of the works examining the mechanism of action of detergent additives has the character of assumptions not always sufficiently founded by experimental data.

The strict washing action of additives P. I. Sanin and coauthors [57] attribute to the ability of detergent additives to disperse insoluble products of aging and incomplete combustion of hydrocarbons of oil and fuel, and the ability to stabilize the suspension of these products in oil. The opinion on the fact that the dispersive and stabilizing action of additives on insoluble products of motor oil determines the washing effectiveness of additives, divides the majority of the other authors.

Many researchers connect the stabilizing action of additives first of all with their ability to be adsorbed on the insoluble particles forming in the oil. However, it is impossible to explain the mechanism of action of certain additives by one adsorptive effect [58]. Many surface active substances forming durable adsorptive films not only do not improve but considerably worsen the washing properties of the oil. It was determined that sulfonates of average molecular weight possess greater adsorptive properties than do the high-molecular sulfonates. Sulfonates of average molecular weight turned out to be worse with an appraisal of their washing and dispersive properties than the high-molecular sulfonates. In the process of the study of barium additives of different structure by methods of electron microscopy and paper chromatography, it is established that barium sulfonate possesses greater ability to disperse products of aging and contamination of oil than that of alkylphenolate and barium dialkyl dithiophosphate.

Investigations showed that between dispersive ability of these additives and their surface activity it is impossible to establish a direct dependence [59]. An analogous conclusion is made on the basis of a comparison of results of the investigation of the dispersive ability of domestic sulfonate additives. B. V. Losikov and A. A. Aleksandrove [60] showed with an investigation of calcium salts of organic sulfonic acids that the stabilizing effect characteristic for these products is in a direct dependence on their molecular weight and stability of their solutions in the oil. As B. V. Losikov and others [61] consider, the behavior of detergent additives can be analogous to the behavior of stabilizers in classical colloidal systems.

The stabilization of carbonaceous suspensions in motor oil by detergent additives can be connected with the anticoagulating action. During collision of two particles of the colloidal system both attractive forces and repulsive forces act. Attractive forces are forces of the van der Woals type, while when forces of repulsion are caused by the electrostatic interaction between charged surfaces of the particles [62]. When Woals attractive forces predominate, the colloidal system is aggregately unstable. With the predominance of electrostatic forces of repulsion the quantity of collisions leading to coagulation decreases, and the stability of the system increases.

Thus it is possible to consider that during operation of the engine electrical properties of surfaces of colloidal particles – products of oxidation of oil and combustion of fuel – essentially affect the stability of their suspensions in oil, which is directly connected with the quantity of deposits forming in the engine. Electrical properties of surfaces of finely dispersed products of oxidation of oil and combustion of fuel depend on properties of surface active substances adsorbed on them, in particular detergent additives. As Brian and Bernelin [63] note, results obtained by different experimental methods show that detergent additives in hydrocarbon solutions form associated colloidal particles, which have a cylindrical or spheric form and, as a rule, are solvated [64]. The quantity of molecules entering into composition of such micelles can be changed from 10 to several hundreds [65, 66]. It is very difficult to establish the critical concentrations of micelle formation of additives in oil. As Zisman and Murphy [67] note, the critical concentration of the formation of micelles by certain sulfonates in hydrocarbon solutions amount to a value of the order of 10^{-6} mole/ℓ, i.e., it is considerably below the critical concentration micelle formation in water systems.

As Bernelin [64], Courtel, and Larbre [68] showed, under conditions of the action of an electrical field in hydrocarbon medium there is observed a directed displacement of associated colloidal particles of detergent additives and also a displacement of the very hydrocarbon medium; in other words, there are observed phenomena of electrophoresis and electro-osmosis. Electrophoresis and electro-osmosis are possible when there exists a potential drop on the phase boundary.

Consequently, on the surface of the particles formed by detergent additives with dissolution in hydrocarbon media, there should exist a double electrical layer. Properties of the double electrical layer of particles of detergent additives in oil will obviously determine the electrical properties of surfaces on which they are adsorbed. The investigations conducted [63, 69, 70] showed that different commodity washing substances impart to carbonaceous particles suspended in a hydrocarbon medium electrokinetic properties which can change depending upon the concentration of the washing substance.

It was possible to establish the relationship between the rate of electrophoresis displacement of particles of suspensions and rate of their coagulation: the higher the speed of electrophoresis, the slower coagulation occurs. Agius and Mulvey [71] showed by their investigations conducted with suspensions of slime, which was obtained from an automotive engine, that some dispersive additives imparted to particles of slime a positive charge and others – negative. They established that with the introduction into suspension of a mixture of additives which separately imparted to the particles of slime charges of a different sign, the stability of suspensions considerably descended.

The stabilizing action of detergent additives can be caused not only by electrical forces appearing between carbonaceous particles in the operating motor oil with adsorption on them of charged micelles of the additive but also can be connected with the stabilizing action of micelles of the detergent additive [72]. An additive in concentration exceeding the critical concentration of micelle formation will form a micellar structure in the oil. Micelles of the additive actively interact with products of oxidation and contamination forming in the oil, as a result of which these products are either concentrated on the surface of the micelles or are absorbed by them. These processes lead to transfer of products of aging and contamination of the oil into a colloidal solution.

Surface active substances containing less than 7-8 atoms of carbon in a molecule are ineffective as solubilizators [73]. The structure of the hydrocarbon radical greatly affects the solubilizing ability of the washing substance.

On the basis of experiments conducted Courtel and Larbre [68] affirm that solutions of detergent additives in motor oils are analogous in their properties to aqueous solutions soaps. In particular, such an analogy, in their opinion, is indicated by micellar structure of solutions of detergent additives, the solubilizing action of their micelles and electro-osmosis and electrophoresis. These authors drew a conclusion concerning the expediency of the use for the study of solutions of detergent additives in oils of experimental methods used for the study of aqueous solutions.

In literature there is noted the ability of detergent additives to wash off deposits already formed from metallic surfaces of parts of the engine and prevent adhesion of deposits owing to the formation of adsorptive layers [74, 75]. In the opinion of Bondi [76], this last property of detergent additives frequently is not given proper importance.

Affirmation of certain researchers about the formation of adsorptive layers on metallic surfaces by particles of detergent additives preventing adhesion of products not soluble in oil [60, 76, 77] remained the hypothesis until there was obtained direct confirmation by our experimental investigation in which detergent additives labeled by a cation and radical [37, 38] were used.

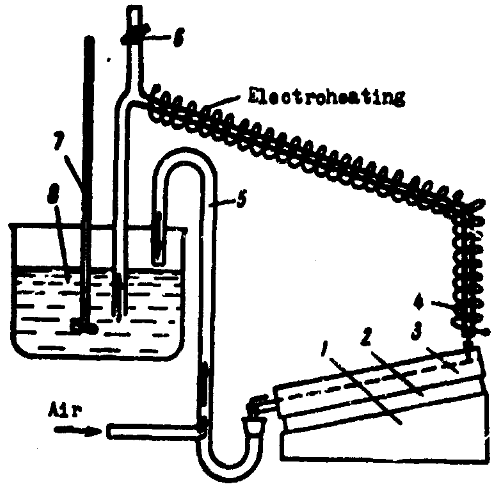

Fig. 16. Diagram of experimental apparatus for tests of detergent and antioxidant properties of motor oils with additives: 1 – support; 2 – thermoelement; 3 – working plate of stainless steel; 4 – capillary tube; 5 – gas lift; 6 – tap for tapping of air bubbles; 7 – mixer; 8 – tested oil.

Investigations were conducted by means of oxidation of oil with a labeled additive in a thin layer on the experimental apparatus [78] whose diagram is shown in Fig. 16. Oil continuously flowed along the surface of a steel plate heated to a temperature of 250°C. The duration of the experiment amounted to 10 h. Upon completion of the experiment quantity of the labeled additive on the surface of the plate with the help of an end-window beta-counter was determined. Figure 17 gives results of the investigation of oil [AS-6] (AC-6) with the additive [VNII NP-370] (ВНИИ НП-370) (calcium alkylphenolate additive of formaldehyde condensation) labeled by isotopes Ca^{45} or C^{14} and also with a mixture of the additive VNII NP-370 with calcium sulfonate additive [PMS] (ПМС).

On the graph results of these experiments are expressed by the quantity of additive on the surface of metal depending upon the concentration of it in oil (calcium content, %). From Fig. 17 it is clear that the detergent additive VNII NP-370 both in pure form and in a mixture with sulfonate additive PMS with all the investigated concentrations formed on the surface of the metal a film into whose composition calcium and carbon entered. Since the quantity of Ca^{45} on the surface of metal is changed little with a change in concentration of the additive in oil, then, apparently, one can assume that the thickness of film formed by the additive on the surface of the metal has a definite magnitude. This magnitude does not depend on the concentration of the additive in oil but is determined only by the quantity of cations or cation micelles,

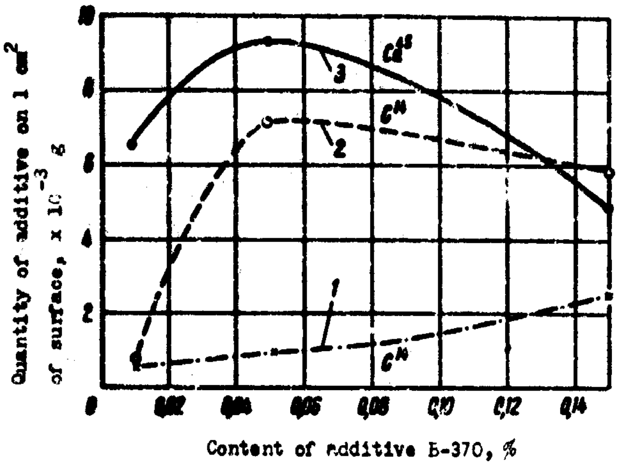

Fig. 17. Quantity of calcium alkylphenolate additive of formaldehyde condensation VNII NP-370 labeled by isotopes Ca^{45} or C^{14} on the surface of the metal depending upon the concentration of additive in the oil: 1 – quantity of additive registered by the radiation of C^{14} for a mixture of additives B-370 + PMS; 2 – quantity of additive B-370 registered by radiation of C^{14}; 3 – quantity of additive B-370 registered by radiation of Ca^{45}.

which can in the form of a monolayer (since the formation of several layers from analogously charged particles is improbable) be placed on the surface of the metal. Thus for the first time it is experimentally proven that certain detergent additives will form films on surfaces of metals.

The use of the experimental apparatus with oxidation of oil in a thin layer on a hot steel plate permitted not only studying certain aspects of the mechanism of detergent action with the help of labeled additives but also radiometrically investigating antioxidant and washing effectiveness of commodity additives to motor oils [79, 80]. The antioxidant properties are estimated by means of measurement of the quantity of lacquer and carbon on the surface of the plate and detergent properties – by means of measurement of the quantity of labeled soot introduced into the oil adhering to the surface of the plate.

As was shown in Fig. 16, the apparatus consists of a working plate 3 made from stainless steel having dimensions of 200 × 600 mm and a thickness of 20 mm. The plate is mounted on a support 1 at an angle of 15° to the horizontal. So that the oil would not flow out along the flat sides of the plates there are made borders 10 mm in height. Heating of the plate to operating temperatures of 250° or 300°C is conducted with the help of a closed thermoelement 2. Oil from cup 8 is fed to the surface of the plate along the capillary thick-walled tube 4 at a definite speed. After spreading along the surface of the plate the oil gets into the glass tube 5 and by an air flow rises into cup 8. Thus the oil circulates about the system during the entire experiment. The speed of the supply of oil from the capillary tube to the surface of the plate is regulated with the help of heating of the tube by an electrospiral. Tap 6 serves for the tapping of air bubbles accumulating in oil. The experiment with constant mixing lasts 5 h at a temperature of the plate of 300°C or 10 h at a temperature of 250°C.

The plate, washed with gasoline and dried, is placed into the instrument for radiometric measurement of the quantity of deposits (mg/cm^2) on the surface of the plate. The instrument shown in Fig. 18 is an end-window Geiger counter and in front of the small window there is mounted the source of β-radiation (isotope Ca^{45} with an activity of about 50 μCi) placed into a copper ampoule with a collimator. The ampoule removes possibility of the falling into the counter of a direct beam β-radiation. The collimator directs the beam of β-radiation to the surface of the plate. Backscattered β-radiation is recorded by a counter with the help of the scaling apparatus "Volna."

The intensity of backscattered β-radiation depends on the distance between the surface of the plate and Geiger counter with the source of radiation fastened to it. The optimum distance between them should provide maximum effectiveness of registration of radiation [81]. To calibrate the instrument there is taken the curve of the dependence of counting rate on the thickness of the covering on plate $N = f(d)$. During calibration, as a covering aluminum foil of different thickness is used. In order not to introduce corrections for disintegration of the source of β-radiation, the calibration curve is constructed in relative values $\frac{N}{N_0}\cdot 100\% = f(d)$. Plotted along the axis of the abscissas are values of the thickness of covering d (mg/cm^2) and along the axis of the ordinates, the ratio $\frac{N}{N_0} \cdot 100\%$, where N_0 is the counting rate with measurement of the plate without covering, and N is the counting rate during measurement of the plate with a covering of different thickness [81].

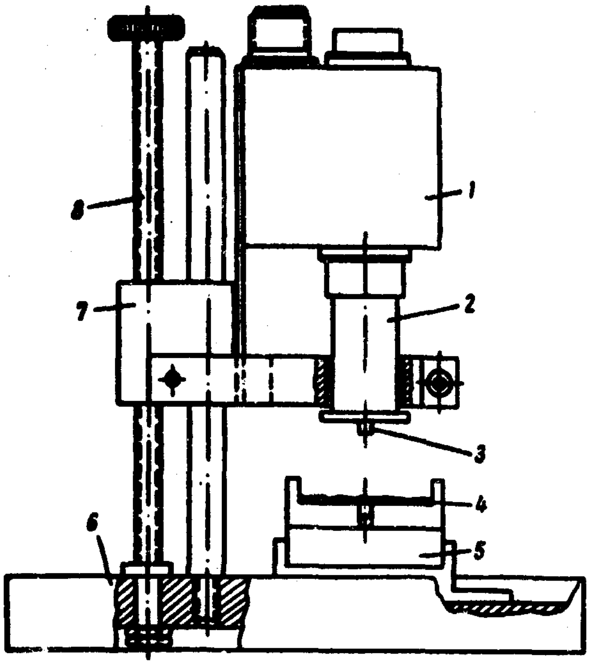

Fig. 18. Diagram of the instrument for determination of the quantity of deposits (lacquer and carbon) on the surface of metal by backscattered β-radiation: 1 – extension unit of radiometric apparatus; 2 – end-window Geiger beta-counter; 3 – copper ampoule with a source of radiation Ca^{45} (activity of about µCi); 4 – layer of deposits of lacquer and carbon; 5 – working plate on the surface of which deposits were formed; 6 – base of the instrument; 7 – mobile connector sleeve; 8 – lead screw.

Multiple tests of different additives showed that with the quantity of deposits formed on the surface of the plate up to 1.0 mg/cm^2 the divergence between results of parallel determinations reaches ±0.25 mg/cm^2 and with a larger quantity of deposits, ±0.5 mg/cm^2.

To determine the quantity of carbon block adhering to the surface of the plate there is conducted a test at which into the oil with the additive there is introduced labeled carbon block [79, 80]. Carbon block of the Micronex type, with a specific surface of 100 m^2/g labeled by radioactive isotope Tl^{204} is used. This isotope was selected because it has a sufficiently great half-life (3.5 years) and possesses only β-radiation with an energy of 0.76 MeV. The weighed sample of carbon block is activated, moistening it by a solution of chlorous thallium (activity of 1-2 µCi) and drying at a temperature of 20°C (for achievement of adsorptive equilibrium). Then the carbon block is washed by distilled water from chlorine ions. The dried radioactive carbon block is introduced into the naphthene paraffin fraction of oil [SU] (СУ) (ratio of carbon block and fraction is 1:5), and several drops of the obtained indicated labeled dispersed system are introduced into the investigated oil, which after this is treated by ultrasonics. Treatment was conducted for three minutes to obtain a stable suspension with power of 1 kW and frequency of 23 kHz.

After testing the oil with labeled carbon block at the assigned temperature of the surface of the plate, the plate is set under the end-window Geiger counter, and with the help of the scaling apparatus "Volna" the quantity of labeled carbon block on the surface of the plate was determined.

Table 9. Results of tests of motor oil AS-9.5 with different antioxidant additives.

Additive and its concentration in oil	Quantity of deposits on the surface of the plate (mg/cm^2) after tests at a temperature of	
	250°C	300°C
0.6% Orobis-267	0	0.45
0.7% Santolube-493	0	5.4
1.5% VNII NP-354	0.05	0.4
1.2% DF-11	0	0.5
2% VNII NP-167	0.5	>8
1.2% B-501	>8	>8
0.6% B-501	>8	>8
1.2% [LZ-317] (ЛЗ-317)	>8	4.6
2% VNII NP-390	2.7	3.35
0.3% Phenyl-α-naphthylamine	1.0	>8
0.005% [PMS-200A] (ПМС-200А)	1.2	0.7

Table 9 gives results of tests of motor oil AS-9.5 with different antioxidant additives. It is clear that tested antioxidant additives possess different effectiveness, and the majority of the additives lose the effectiveness with an increase in temperature of the surface of the plate from 250° to 300°C.

Table 10. Results of tests of motor oil AS-9.5 with different concentrations of antioxidant additives.

Additive	Concentration of additive in oil, %	Quantity of deposits on surface of the plate, mg/cm^2	Additive	Concentration of additive in oil, %	Quantity of deposits on surface of the plate, mg/cm^2
Santolube-493	0.25	2.05	VNII NP-167	1.50	3.3
	0.50	1.15		2.00	0.5
	0.70	2.0		3.00	1.15
	1.20	>8.0			
			DF-1	0.10	6.2
VNII NP-167	0.50	6.2		0.50	4.2
	1.00	3.8		1.00	3.7
				2.00	>8.0

[DF-1 = ДФ-1]

Table 10 gives results of tests at a temperature of the surface of the plate of 250°C of three antioxidant additives introduced in different concentrations into oil AS-9.5.

From Table 10 it is clear that there exist optimum concentrations of these additives in oil at which a minimum quantity of deposits on the plate is observed.

Table 11 gives results of tests of motor oil AS-9.5 with different concentrations of import additives of firms Monsanto and Orobis. From Table 11 it is clear that the additive of the firm Orobis possess higher detergent effectiveness than that of additive Monto-702. With an increase in the concentration of additives of the firm Orobis in oil, their detergent effectiveness is increased.

The examined radioactive tracer method permits estimating both the antioxidant and natural detergent action of additives to motor oils.

Table 11. Results of tests of a motor oil with different concentrations of additives.

Additive	Concentration of additive in oil, %	Quantity of deposits on surface of the plate, mg/cm^2	Quantity of labeled carbon black on surface of the plate, imp/min
Monto-702	1.80	>8.00	480
	4.50	0.60	110
	9.00	0.55	60
	18.00	0.85	170
Orobis-205	1.10	2.65	320
	2.75	0.15	0
	5.50	0.20	0
	11.00	0	0
Orobis-2112a	1.70	1.05	250
	4.25	0.40	0
	8.50	0.05	0
	17.00	0.20	0
Orobis-218a	2.50	0.20	100
	6.25	0.05	25
	12.50	0	0
	25.00	0.15	0

Investigation of the Mechanism of Natural Detergent Action of Additives to Oils

By the natural detergent action of additives we understand their ability to prevent adhesion of carbonaceous products of aging and contamination of oil toward the surface of the metal and to wash off the deposits already formed. From our point of view, the natural detergent action is one of the mechanisms of action of detergent additives which plays a no less important role in providing cleanness of parts of an engine than, for example, that of the stabilizing action.

According to our hypothesis, the mechanism of natural detergent action of additives is based on the sorption of ions or ionic micelles of an additive on the surface of carbonaceous particles (products of the combustion of fuel and oxidation of oil) and metallic parts of an engine. Sorption leads to the creation of analogous electrostatic charges and to the repulsion of particles from one another and from metallic surfaces. From this hypothesis it follows that the natural detergent action should be more effective the higher the electrical conductivity of the additive solution in oil. Such a conclusion is experimentally confirmed by us with a comparison of results of the determination of electrical conductivity of solutions of different detergent additives in motor oils and results of the determination of the quantity of labeled carbon black in scale with a test of the same additives on the apparatus with a slanted plate: as can be seen from Fig. 19, the higher the electrical conductivity of additive solution in oil, the less the quantity of labeled carbon black on the surface of the plate.

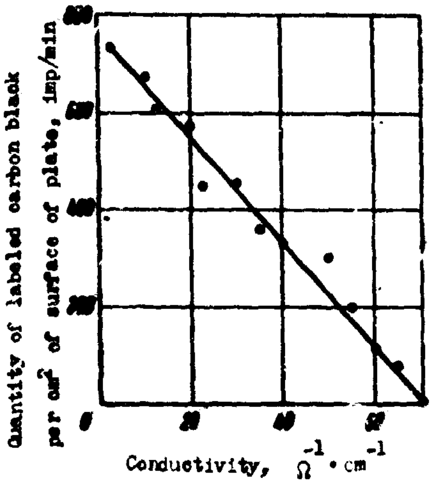

Fig. 19. Dependence of the quantity of labeled carbon black adhering to the surface of the slanted heated plate on the conductivity of oxidizable oils with additives.

As it was shown above, the presence in internal combustion engines of electrical fields with an intensity to several thousands of volts per centimeter should have considerable influence on the effectiveness of the detergent action of additives. In connection with this we studied the mechanism of the natural detergent action of additives to motor oils under conditions of the electrical field [82-84].

To study the mechanism of natural detergent action the behavior of the model charged dispersed phase in the electrical field[1] artificially created in the oil was studied. As such a model dispersed phase there was used, as in experiments on the apparatus with a slanted plate, carbon black (labeled by thallium-204) of the type Micronex.

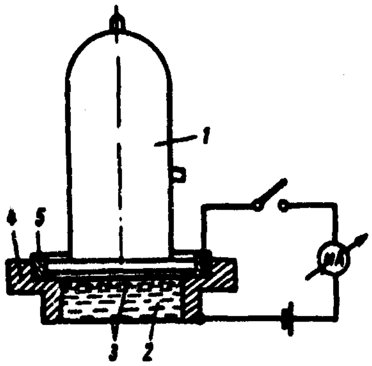

Fig. 20. Diagram of the laboratory experimental apparatus for electrokinetic and radioactive tracer investigations: 1 – end-window beta-counter MST-17; 2 – oil; 3 – foil; 4 – plastic vessel; 5 – cover.

A diagram of the laboratory apparatus on which there were investigated a shift in the dispersed phase under conditions of action of the electrical field and influence of different additives on the behavior of dispersed phase is shown in Fig. 20. The cylindrical plastic vessel with an internal diameter of 20 mm (corresponding to the diameter of the window of the end-window Geiger counter [MST-17] (MCT-17)), a height of 10 mm and bottom of aluminum foil was filled with the oil to be investigated. On the vessel a plastic cover with a bottom of aluminum foil 0.02 mm thick was installed. Fastened to the cover was a counter MST-17 connected to a radiometric self-recording apparatus. To the aluminum foil of the bottom and cover was fed a voltage from the high-voltage rectifier Orekh, and the current was measured by a microammeter M-95. Measurements were taken at a temperature of the oil of 20 ± 1°C. To obtain a stable suspension a sample of oil with introduced carbon black (10 g) was treated for 3 min by ultrasonics.

Figure 21 gives automatically recorded diagrams characterizing the rate of deposit of labeled carbon black on the surface of the upper electrode at different electric field strengths. The rate was estimated by the slope angle of the curve of accretion of radioactivity to the time axis and was expressed in pulses per second per hour. From Fig. 21 it is clear that the labeled carbon black Micronex, introduced into oil AS-6 without an additive, was separated out on the anode and, consequently, had a negative electrical charge. In these experiments it was established that the formation rate of deposits is proportional to the concentration of carbon black in the oil and electric field strength.

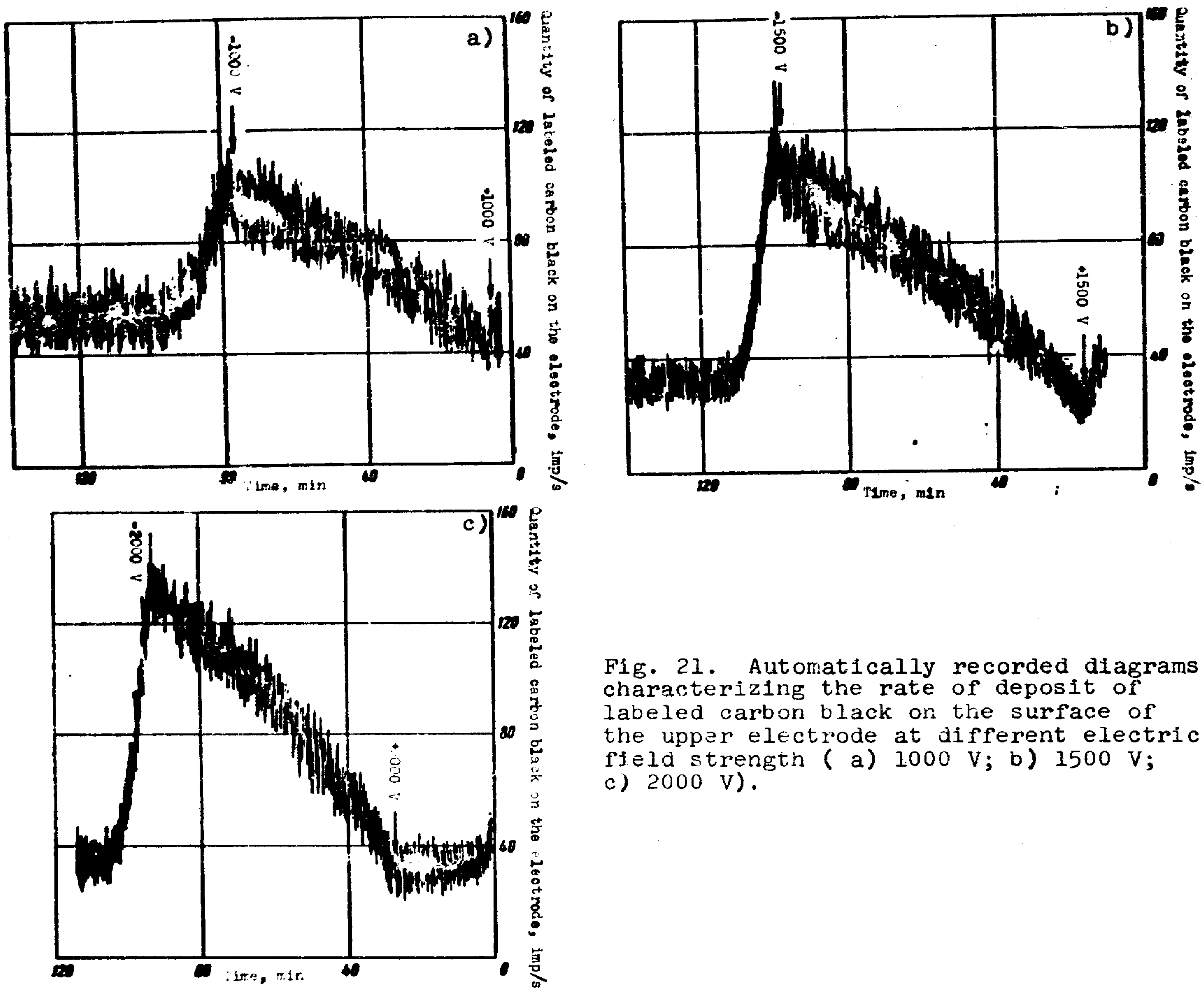

Fig. 21. Automatically recorded diagrams characterizing the rate of deposit of labeled carbon black on the surface of the upper electrode at different electric field strength (a) 1000 V; b) 1500 V; c) 2000 V).

Table 12. Influence of dithiophosphate additives on the formation rate of deposits of carbon black under the action of an electrical field.

Additive	Concentration, %	Sign of charge or carbon black	Formation rate of deposits, (imp/s)/h	Total activity on the electrode, imp/s
Without additive	-	-	120	>200
VNII NP-353	0.01	-	500	>200
	0.10	-	160	>200
	1.00	+	150	>200
	10.00	+	60	>200
DF-1	0.01	-	390	>200
	0.10	-	380	>200
	1.00	-	200	70
	10.00	+	130	0
DF-11	0.01	-	390	>200
	0.10	-	480	>200
	1.00	-	250	>200
	10.00	+	60	>200
Santolube-493	0.05	-	300	>200
	0.50	-	300	>200
	1.00	-	350	

The investigations conducted showed that even in the absence of products of oxidation of oil (such as hydroxy acid and asphaltenes) and at room temperature carbonaceous particles, under the impact of an electrical field of the same intensity as that in an engine, are able to form on the surface of the metal of deposition.

With the help of the developed methods there was investigated the influence of different additives introduced into motor oil AS-6 on the formation rate and quantity of deposits under conditions of action of an electrical field. Into investigated samples of oil AS-6 carbon black was introduced in a concentration of 5 mg/mℓ, and the suspensions were treated by ultrasonics. Tables 12 and 13 give characteristic results of a series of investigations of certain types of additives at a field strength of 2500 V/cm. As can be seen from Table 12, the introduction into the oil of dithiophosphate additives in small

Table 13. Influence of calcium sulfonate and alkylphenolate additives on the formation rate of deposits of carbon black under the action of an electrical field.

Additive	Concentration, weight, %	Sign of charge of carbon black	Speed of electrophoresis, (imp/s)/h	Total activity on electrode, imp/s
VNII NP-370	0.1	-	140	>200
	0.1	-	147	>200
	0.1	-	141	>200
	0.5	-	130	>200
	0.5	-	122	>200
	0.5	-	130	>200
	0.1	-	240	>200
	0.1	-	235	>200
	0.1	-	230	>200
	0.2	-	270	120
	0.2	-	260	115
	0.2	-	278	123
	0.3	-	290	30
	0.3	-	286	31
	0.3	-	290	33
	0.4	-	310	40
	0.4	-	300	40
	0.4	-	305	30
	0.5	-	330	30
	0.5	-	334	38
	0.5	-	331	32
	1.0	-	400	10
	1.0	-	396	5
	1.0	-	392	11
Monto-702	0.01	-	100	50
	0.01	-	91	65
	0.01	-	104	50
	0.1	+	50	0
	0.1	+	45	0
	0.1	+	50	0
	1.0	+	540	0
	1.0	+	570	0
	1.0	+	538	0

concentrations leads to an increase in the formation rate of deposits of carbon black on the anode. An increase in the concentration of these additives in oil in certain cases leads to a recharge of the carbon black, but the formation rate of the deposits remains considerable. Only with the introduction into the oil of additive [DF-1] (ДФ-1) in sufficiently great concentrations is there observed a deceleration of the formation of deposits and considerable lowering in the total quantity of carbon black deposited on the electrode.

From the given data it can be concluded that the investigated dithiophosphate additives are impossible to use for effective lowering of the quantity of deposits under conditions of an electrical field, with the exception of additive DF-1 in large concentrations. In this case, and also with the investigation of certain detergent additives whose results are given in Table 13, there is observed a different form of the automatically recorded diagrams than those shown in Fig. 21. For example, Fig. 22 shows a diagram recorded during an investigation of oil AS-6 with 9% additive Monto-702 from which it is clear that in the presence of this additive in oil the formation of deposits of carbon black on the electrodes does not occur. At the same time there are observed stepwise changes of the recording on the diagram at the time of the voltage feed or change in polarity of electrodes.

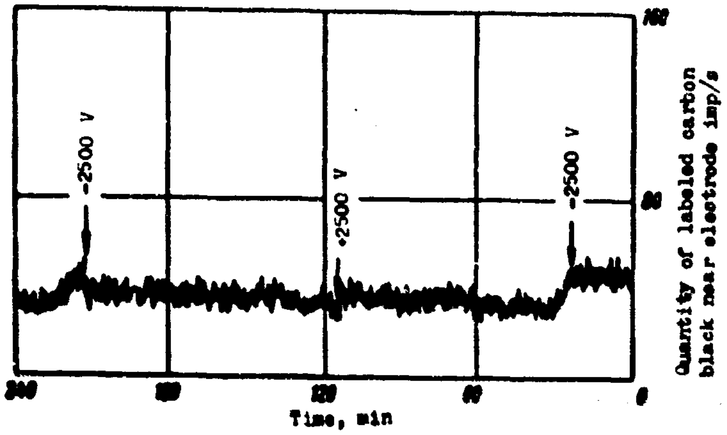

Fig. 22. Automatically recorded diagram characterizing the behavior of labeled carbon black during the investigation of oil with 9% of additive Monto-702.

Separated from the oil by an aluminum foil 0.02 mm thick, the end-window Geiger counter MST-17 is able to record β-radiation of thallium-204 (with energy of 0.7 MeV) not only from particles of labeled carbon black adhering to the surface of the foil but also from carbon black being in the volume of oil at a distance of up to 3 mm from the counter. Therefore, the counter can record a change in the mean concentration of labeled carbon black in a volume of oil during its electrophoresis shift. On diagrams obtained during the investigation of oil without additives (see Fig. 21) both processes – adhesion of labeled carbon black to the surface of the foil and its electrophoresis shift – are reflected by one general curve of the increase in radioactivity. If there is no adhesion of carbon black to the surface of the foil (see Fig. 22), a stepwise change of recording on the diagram reflects a change in the mean concentration of labeled carbon black in the space adjacent to the electrode due to rapid electrophoresis shift of the carbon black, having obtained additional high charge with sorption on its surface of particles of additive from the oil.

As can be seen from Table 13, in the absence of adhesion of carbon black, the greater the speed of electrophoresis the higher the concentration of additive Monto-702 in oil, i.e., the higher the electrical conductivity of the solution. The increase in speed of electrophoresis with an increase in the size of the charge of dispersed phase in hydrocarbon media is noted also in works of Garner [86] and Courtel with coauthors [87].

Thus certain detergent additives prevent the formation of deposits of a charged dispersed phase on the electrodes.

It is possible to assume that the mechanism of action of additives in these conditions is connected with the formation by charged particles of an additive in the zone of every electrode of electrostatic barriers, which prevent separation of carbon black on the electrodes. Investigations conducted with labeled isotope Ca^{45} by alkylphenolate additive VNII NP-370, confirmed such an assumption.

Experiments were conducted on the laboratory apparatus whose diagram is shown in Fig. 20. The plastic vessel was filled with oil with labeled additive VNII NP-370, and with help of radiometric instrumentation the shift in particles of additive by radiation of calcium-45 was recorded. It was established that under the action of the electrical field, particles of the additive rapidly shifted to the upper electrode independent of the sign of its charge, and then the concentration of additive on the electrode and in the space near the electrode was increased.

The fact that irrespective of the sign of charge of the upper electrode there was observed an increase in the quantity of calcium-45 near its surface indicated the fact that in the solution of the additive in oil there are positively and negatively charged particles of the additive VNII NP-370 containing calcium-45. Analogous results are obtained and during the investigation of the labeled sulfonate additive PMS and composition of labeled additives PMS and VNII NP-370.

An increase in the concentration of the additive in the space near the electrode creates, obviously, an electrostatic barrier, preventing separation on the electrode of a charged dispersed phase. Formation by additives of an electrostatic barrier was observed only in those cases when the concentration of the additive was sufficient so that particles of it occupied during sorption the whole surface of the introduced dispersed carbon black and also were separated in the space near the electrode. With smaller concentration of the additive there occurred intense deposition of carbon black on the electrodes. Thus Fig. 23 gives experimental data on the deposition of soot on electrodes from a solution of oil without an additive and from a solution with an insufficient concentration of additive. It is clear that the quantity of recorded carbon black and speed of its separation is greater in case b (oil with an insufficient quantity of additive). These data are obtained with the help of the experimental apparatus shown in Fig. 24. The polished ring 2 of stainless steel revolves from an electric motor through a belt transmission at a speed of 10-12 r/min, and this ring is one electrode. The other electrode is bath 1 of stainless steel in

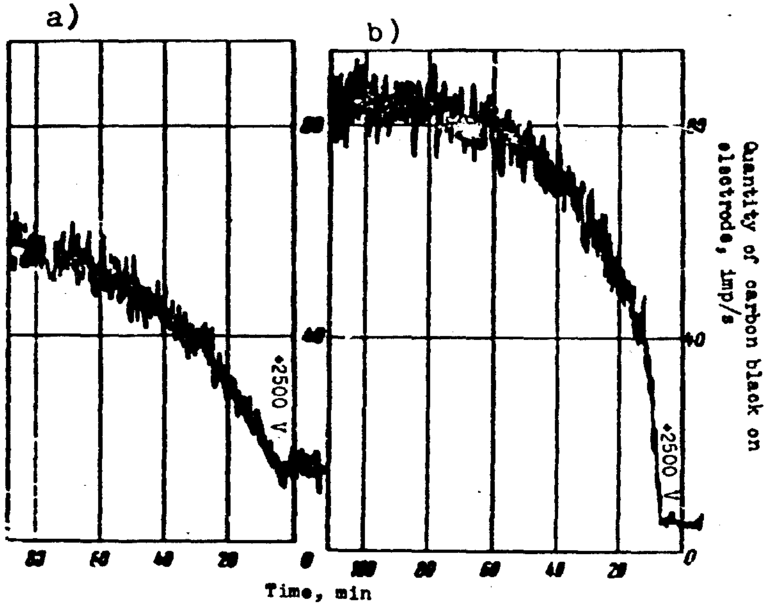

Fig. 23. Automatically recorded diagram of separation out of labeled carbon black on the upper electrode under the action of an electrical field: a) from oil AS-6 without additive; b) from oil AS-6 with additive (1.8% Monto-702) the quantity of which is insufficient for blocking of the separation of carbon black.

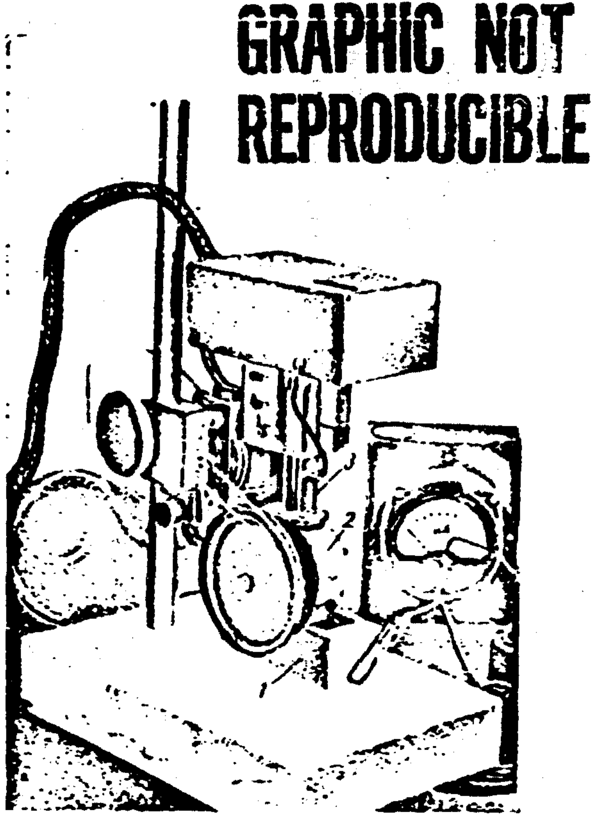

Fig. 24. Experimental apparatus for investigation of the formation of deposits under conditions of the action of an electrical field.

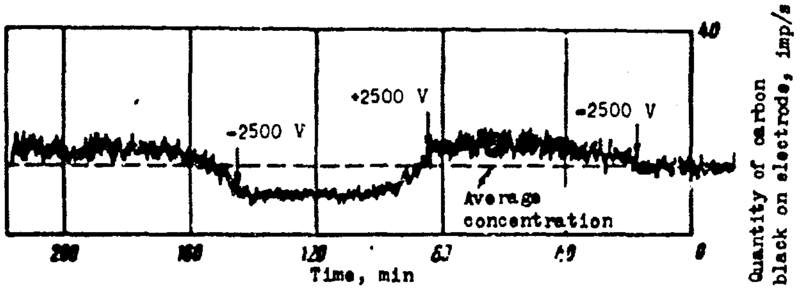

Fig. 25. Automatically recorded diagram reflecting the behavior of labeled carbon black under conditions of action of an electrical field with a surplus of additive (18% Monto-702) in oil AS-6.

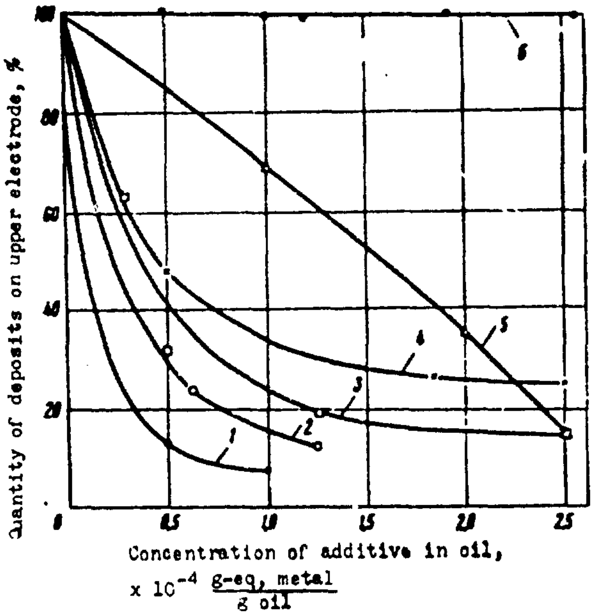

Fig. 26. Influence of the concentration of different additives on the quantity of deposits of labeled carbon black on the upper electrode: 1 – ASK; 2 – PMS + + B-370; 3 – Monto-702; 4 – Orobis-2112a; 5 – MASK; 6 – PMS and SK-11.

which the oil to be tested is filled with a radioactive dispersed phase treated by ultrasonics. Ring 2 was dipped in oil to a depth of not more than 1 mm. With the help of the end-window beta-counter 3 connected to the self recording radiometric installation the quantity of labeled dispersed phase adhering to the ring was continuously recorded. Figure 25 gives results of the experiment on oil with 18% additive of Monto-702 with a concentration of carbon black in the oil of 10 mg/g. With such relationship of concentration of dispersed phase and additive there was not observed separation out of labeled carbon black on electrodes. Analogous results are obtained with the investigation of other additives.

Figure 26 shows the influence of concentration of different additives in oil on the quantity of deposits of labeled carbon black on the upper electrode under conditions of action of an electrical field. Investigations are conducted according to the diagram shown in Fig. 20; the quantity of deposits of labeled carbon black on the upper electrode during a test of oil without an additive is accepted as 100%. From Fig. 26 it is clear that the most effective in preventing formation of deposits is the additive alkyl salicylate calcium [ASK] (АСК), and sulfonate additives PMS and [SK-11] (СК-11) in the examined conditions of investigations even in maximum concentrations do not lower the quantity of deposits of carbon black on the electrode. Apparently, the effectiveness of action of these additives is connected not with the formation of electrostatic barriers but with the solubilization of products of aging and contamination of oils [72].

There is an investigation of oil with additives with radioactive carbon black dispersed in it with the help of ultrasonics on a laboratory centrifuge at 1500 r/min. The oil was diluted by Galosha [Editor's NOTE: This is a rubber solvent (naphtha)] in a ratio of 1:2. Checking for the loss of the dispersed phase was carried out in periodic measurement of radioactivity of the upper layer of the centrifuged suspension. From Fig. 27, on which results of these experiments are given, it is clear that the greatest stability of suspension was provided by the additive PMS.

From Figs. 26 and 27 it is clear that additives to motor oils possessing the most effective natural detergent action are not able to stabilize the suspensions of finely dispersed products of contamination of oils, whereas the most effective stabilizing additives do not provide natural detergent.

Such results of laboratory investigations led to the conclusion that optimum properties should possess compositions of additives one of which provides natural washing and the other, stabilizing action. During a test of an oil with such compositions of additives on full-scale overloaded diesel engines, good results were obtained.

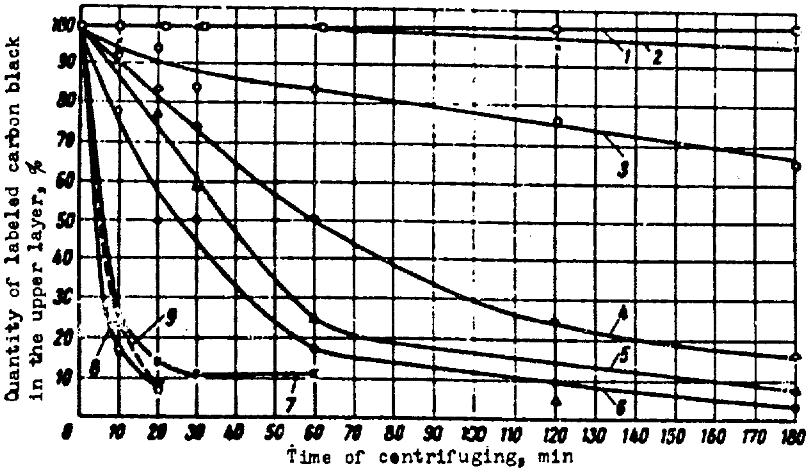

Fig. 27. Results of the determination by means of centrifuging of the suspension of labeled carbon black in oil AS-6 with different additives: 1 — 0.42% PMS; 2 — 0.5% SK-11; 3 — 0.9% Monto-702; 4 — 0.85% Orobis-2112a; 5 — 0.21% PMS + 0.65% B-370; 6 — 1.2% [NG-104] (НГ-104); 7 — 1.3% B-370; 8 — 1.6% ASK; 9 — 0.6% MASK.

Thus the investigations conducted showed that the mechanism of action of certain detergent additives under conditions of the electrical field is connected with the sorption of charged particles of the additive on sooty products and with the preventing of settling out of these products due to the creation of raised concentration of charged particles of the additive in the zone of the electrodes.

Researches according to the diagram shown in Fig. 20 were conducted: in fresh oil and oil worked through a diesel engine there were introduced different additives and the same quantity of labeled carbon black. It was determined that for preventing the separation on the electrode of labeled carbon black from the fresh oil there were required considerably smaller concentrations of additives than for preventing of separation of the same quantity of carbon black from oils having worked in an engine. Thus for fresh motor oil 9% of the additive Monto-702 was sufficient, and for the same oil having worked in a diesel engine for 25 h there was required 30% of the same additive. Analogous results are obtained for all other investigated additives. This permits drawing the conclusion that the above-stated conclusions concerning the examined mechanism of action of detergent additives, obtained during the use of labeled carbon black as a model dispersed phase, can be extended to other products of contamination of oil from which deposits in the engine will be formed.

It is known that the mechanism of the natural detergent action most clearly appears in a water media where the role of the detergent agent leads basically not to the preventing of settling out of contaminations on the surface but to the washing of already formed contaminations with which Coulomb forces have considerable importance [88]. It was determined that solutions of certain additives in motor oils are also able to wash off the already formed deposits of carbon black. This was revealed with the carrying out of experiments on the same experimental apparatus (see Fig. 20): at first from oil without an additive containing labeled carbon black there was separated out carbon black on the surface of the upper electrode with the formation of deposits under the action of an electrical field of 2500 V/cm, and then the vessel was filled with the oil with the investigated additive, and at the same sign and magnitude of charge of the upper electrode a change in the quantity of labeled carbon black on its surface was recorded. Figure 28, for example, gives automatically recorded diagrams characterizing the formation of deposits of labeled carbon black on the surface of the upper electrode from oil AS-6 without an additive and the washing of these deposits by oil AS-6 with 1.8% additive of Monto-702.

From Fig. 28 it is clear that deposits of carbon black were intensively washed off from the surface of the electrode. An analogous effect is obtained with the investigation of certain other additives (Table 14). It should be noted that the effect of washing of deposits of carbon black was ensured by solutions of additives in oils possessing relatively high electrical conductivity.

An increase in electrical conductivity of the solution of additive in oil led to an increase in effectiveness of the natural detergent action. Thus with the introduction of 5% phenol into a

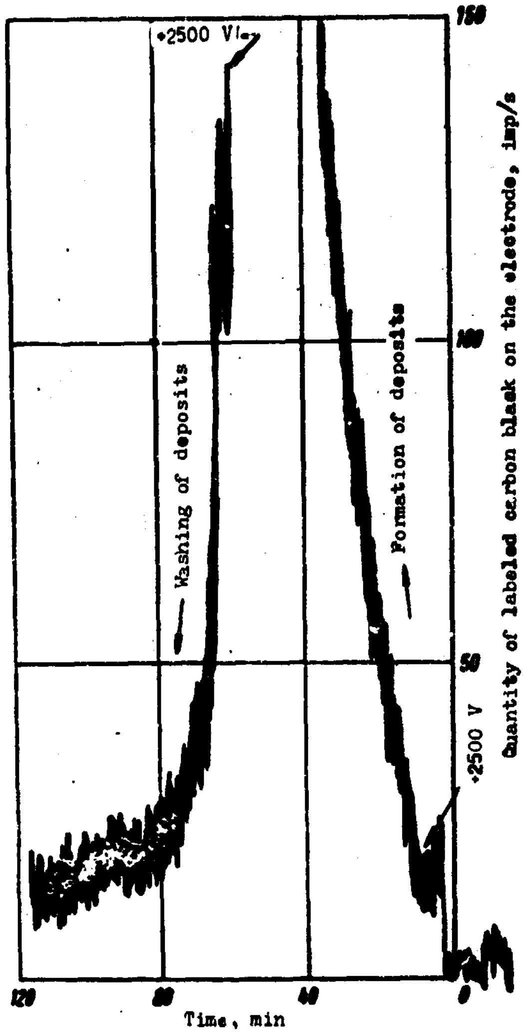

Fig. 28. Automatically recorded diagrams characterizing the formation of deposits of labeled carbon black on the surface of the upper electrode from oil AS-6 without an additive and washing of these deposits by oil AS-6 with 1.8% of additive Monto-702.

Table 14. Results of the investigation of the effect of washing of deposits of carbon black by certain additives.

Additive and its concentration in oil AS-6	Effect of washing	Additive and its concentration in oil AS-6	Effect of washing
Without additive	Absent	1.2% MASK	Present
1.9% Monto-702	Present	2.5% Orobis-2054	"
1.7% Orobis-2112a	"	2.4% Orobis-218a	"
0.42% PMS + 1.8% B-370	"	1.8% Monto-613	"
2.6% B-370	"	2.5% NG-104	Absent
0.84% PMS	Absent	2.4% B-360	"
3.4% Ц-339		1.2% IP-22K	Present
1.7% Ц-339 + 0.42% PMS	Present	1.6% ASK + 0.42% PMS	"
3.2% ASK			

[NG-104 = НГ-104, IP-22K = ИП-22К]

solution of PMS additive in oil AS-6 there appeared the effect of washing of the carbon black by this solution. With the introduction of phenol the electrical conductivity of the sulfonate additive increased 10 times; the solution of 5% phenol in oil AS-6 did not give an effect of washing. However, the sufficiently effective washing of deposits of carbon black under conditions of the electrical field provided certain additives whose solutions in oil AS-6 possessed comparatively low electrical conductivity (VNII NP-370, Orobis-218a, [IP-22K] (ИП-22К)). Consequently, the determination of natural washing effectiveness of additives by their electrical conductivity in oil is insufficient; it is important to estimate not only the charge of particles but also their dimension and structure.

Investigation of Relative Dimensions and Charges of Particles Formed by Washing Additives in Oils

The purpose of the conducted investigations was to show that the electrical conductivity of solutions of detergent additives in motor oils is caused by the motion of charged particles of additives in the electrical field. For this the dependence of conductivity of oils AS-6 and [MS-20] (MC-20) (i.e., of oils of different viscosity) with 3.6% of additive Monto-702 on the temperature of the oil was determined. With a temperature rise there was observed an increase in conductivity of oils due to a decrease in their viscosity, and at equal temperature oil of lesser viscosity has a greater electrical conductivity. This indicated that the electrical conductivity of oils is caused by a shift in charged particles of the additive Monto-702. Leading to the same conclusion were results of the determination of the dependence of conductivity of solution of the additive Monto-702 in paraffin on temperature: at the temperature of fusion of the paraffin the conductivity of the solution was intermittently increased. Analogous results are obtained with measurement of the conductivity of the solution of the same additive in solid and liquid benzene.

Experiments were conducted whose purpose was to check whether the particles, charge carriers, are ions of metal or they constitute larger charged particles. Placed into a glass beaker was a coaxial glass tube with a diameter of 20 mm fastened in the support. The tube had a bottom of organic semipermeable partition 20 mm from the bottom of the beaker. The tube was filled with oil AS-6 with 10% additive PMS or 10% PMS + 7.5% VNII NP-370. The additive PMS labeled by the radio isotope Ca^{45} was used. The beaker was filled with oil AS-6 without additives whose radioactivity and electrical conductivity were periodically measured during 42 twenty-four hour periods; there was also measured simultaneously the electrical conductivity of oil with additives filled in the tube. It was established that radioactivity in oil without an additive does not appear, and the electrical conductivity of this oil and oil with additives is not changed; this indicated that the particles - charge carriers - do not pass through the semiimpenetrable partition. Analogous results are obtained with the carrying out of electrodialysis of different additives in an electrical field with an intensity of 800 V/cm during 40 hours. These experiments show that the particles - charge carriers - are not ions of metal but are charged colloidal particles.

Leading to the same conclusion were results of experiments set with the introduction of zeolites of the "X" class (dimension of input channels 10 and 13Å) in oil AS-6 with $25.7\%^{2}$ of the additive B-370, labeled isotope Ca^{45}, or $30\%^{2}$ of additive B-370, labeled C^{14}, and also their mixtures with 4.8% of additive PMS; there was not observed a change in radioactivity and electrical conductivity of oils with additives after removal of zeolites from them which were contacted with the oils for 48 hours.

To determine the relative dimension and charge of colloidal particles in the oils with detergent additives there was investigated their shift from layer of oil with additive to a layer of oil without additive under the action of an electrical field on the same experimental apparatus whose diagram is given above in Fig. 20. Displacement of particles was recorded by microammeter according to the accretion of current in the circuit. The vessel was filled with oil with the investigated additive in such a quantity that the height

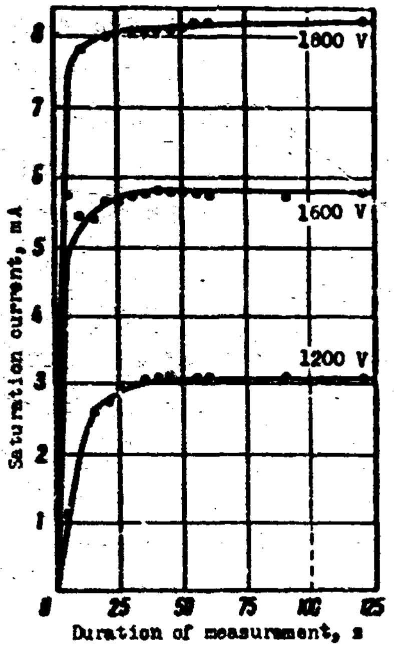

Fig. 29. Electrokinetic curves obtained during investigation of oil AS-6 with 18% of additive Monto-702 with different electric field strengths.

of layer was 5 mm, and above this layer the same oil without additive with a thickness of the layer also at 5 mm was filled. Measurements were taken at a temperature of the oil of 20 ± 1°C at different voltages and different concentrations of additives. Figure 29 gives results of measurements on oil AS-6 with the additive Monto-702 which are typical for all investigated additives. As can be seen from Fig. 29, curves of accretion of the current with time have two clearly expressed segments: the segment of growth and segment of constant values. The growth segment is connected with the nonstationary motion of charged particles: the steepness of it (angle of inclination) is determined by dimensions of the particles — charge carriers. The constant value $I_H = f(E)$ is determined by the quantity of charges brought to the electrodes per unit of time with the motion of the particles at a constant speed. In analyzing the obtained experimental data, it is possible to estimate the comparative dimensions and charges of particles of different detergent additives. For this a graph is plotted in these coordinates: voltage fed to the electrodes (in volts) and magnitude of saturation current (in microamperes). Figure 30 gives, for example, generalized results of such investigations on oil with the additive Monto-702. It is clear that with a growth in the magnitude of the electrical field E there

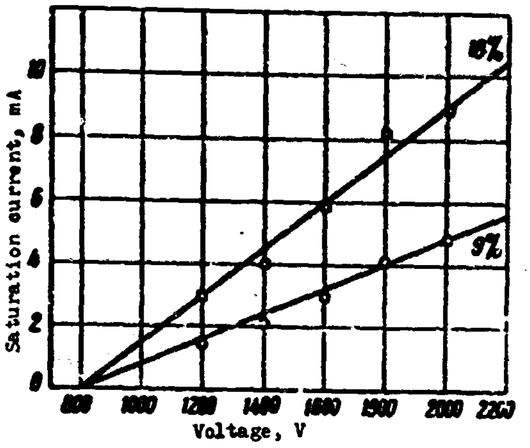

Fig. 30. Dependence of saturation current on the intensity of applied electrical field for oil AS-6 with the additive Monto-702.

is a linearly increase in the recorded saturation current $I_H = f(E)$. Extrapolation of the straight line $I_H = f(E)$ up to the crossing with the axis of abscissas permits determining the E_0, the electric field strength creating the minimum force necessary for overcoming the inertia of particles in the given conditions. Consequently, the quantity E_0 characterizes the comparative dimensions of the particles – charge carriers for oils with different detergent additives with an identical equivalent electrical conductivity of their solutions in oils. Thus a comparison of results of investigations of an oil with additives Monto-702, Orobis-2112a and compositions of additives VNII NP-370 + PMS showed that at close values of magnitudes of the saturation current, i.e., with close equivalent electrical conductivity, the particles, charge carriers of additives Orobis-2112a and Monto-702, have lesser inertia, i.e., smaller dimensions than those of particles of compositions of additives VNII NP-370 + PMS.

At the same time the angle of inclination of straight lines $I_H = f(E)$ characterizes the comparative charge in particles of different additives with their equivalent concentration in oil, i.e., the greater the angle the greater the charge possessed by the particles of the additive. Thus it is possible to assume that additives forming with dissolution in oil particles of small dimensions (i.e., additives characterized by a small value of E_0) which possess a high charge [large value of the angle of inclination $I_H = f(E)$], should possess the best natural detergent properties, since the greatest mobility of such particles (as a result of thermal motion), in absence of an electrical field, and their high charge should lead to a more intense sorption of them on carbonaceous particles and other finely divided products. To check this assumption electrical conductivity of solutions of different additives in oil AS-6 was determined before and after contact with different finely divided products, which completely separated from the oil during filtration or centrifuging. Results of these determinations are given in Table 15. In this table in the last column, the relative change in conductivity in percent, characterizing the ability of the additive to be sorbed, is given. From Table 15 it is clear that the contact of the additives with different (in their nature) finely dispersed products leads to removal from the solutions of a considerable part of the carriers of electrical charge.

Results of investigations given in Table 15 confirmed the assumption expressed above about the fact that charged particles of additives characterized by small values of E_0, possessing small inertness and, consequently, great mobility in the absence of an electrical field, should possess greater comparative ability to be sorbed than the particle with large values of E_0.

From data of Table 15 it is clear that a decrease in the concentration of the additive in oil led to an increase in the relative quantity of sorbed particles and also that the quantity of sorbed additive depends on the temperature of the oil during contacting with the sorbent. The dependence of the quantity of sorbed additive on the temperature of the oil during contacting with the sorbent is shown in Fig. 31 for solutions of the additive Monto-702 and composition of additives VNII NP-370 + PMS. Equivalent electrical conductivities of these solutions have similar values. From Fig. 31 it is clear that the quantity of sorbed additive was increased with a temperature rise in the oil. Inasmuch as the quantity of sorbed charged particles of the additive increases with an increase in temperature, the conclusions with respect to the mechanism of action of additives (founded on the sorption of charged particles of the additive), drawn according to data of experiments at a temperature of the oil of 20°C, should be correct for temperatures of oil in

Table 15. Results of experiments on sorption of additives from solutions in oil AS-6 on different finely dispersed products.

Additive in oil	Sorbent	Quantity of sorbent, g per 50 g of oil	Conditions during constant mixing by mechanical mixer		Conductivity		Relative change in conductivity, %
			temperature, °C	time, h	up to contact with sorbent	after contact with sorbent	
7.5% B-370 + 2.4% PMS	Power of iron oxide	2,0	100	6	77,5	3,1	96,0
The same	Micronex carbon black	2.0	100	6	77,5	10,4	86,8
»	Silica gel	2,0	100	6	77,5	14,7	81,0
7.5% B-370 + 4.8% PMS	Micronex carbon black	2,0	100	6	115,0	59,0	49,0
The same	The same	2,0	20	6	115,0	100,0	12,8
»	Diatomaceous earth	16,0	20	1	115,0	25,6	77,9
10% Monto-702	» »	16,0	20	1	67,0	8,8	86,8
9% Monto-702	» »	16,0	20	1	30,1	3,3	89,1
4.5% Monto-702	» »	16,0	20	1	18,5	0,74	96,0
1.8% Monto-702	» »	16,0	20	1	7,4	0,08	98,9

real engines.

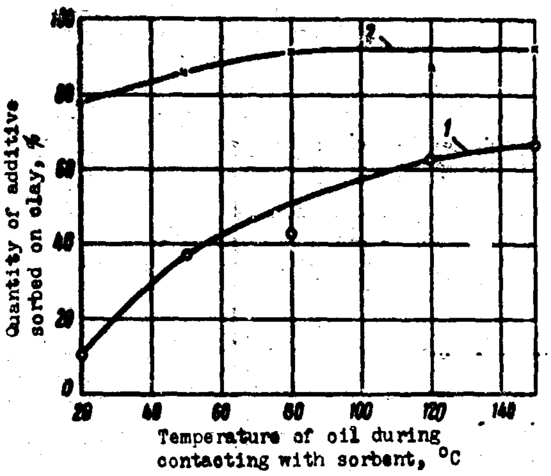

Fig. 31. Dependence of the quantity of sorbed additive on temperature of oil during contacting with the sorbent:
1 – 13% B-370 + 4.2% PMS;
2 – 18% Monto-702.

The results of investigations mentioned above showed that solutions in oils of compositions of additives VNII NP-370 + PMS, possessing high equivalent electrical conductivity, at the same time have larger dimensions of particles than those of investigated solutions of additives Monto-702 and Orobis-2112a. In connection with this it was possible to expect that solutions of the indicated compositions of additives in oils can be less stable than solutions of additives Monto-702 and Orobis-2112a. To check the stability of solutions of the indicated additives in oils under the action of the field of force centrifuging solutions in oil AS-6 diluted by "Galosha" in a ratio of 2:1 were conducted. Solutions were centrifuged consecutively at rates of 5000, 12,000, and 25,000 r/min for one hour with each number of revolutions. Before and after centrifuging the electrical conductivity of solutions by the change in current under conditions of room temperature was estimated.[3] Results of these investigations are given in Table 16. As can be seen from the table, the solution in oil of additive Orobis-2112a, characterized by the least value of E_0, proved to be the stablest: electrical conductivity of the solution did not change after centrifuging at a rate of 25,000 r/min, whereas the additive Monto-702 completely settled out during centrifuging at a rate of 25,000 r/min, and the composition of additives B-370 and PMS was the least stable.

Table 16. Results of the determination of comparative stability of solutions of additives in oils under the action of the field of force.

Investigated additive	E_0, V	Electrical conductivity of solution, %			
		up to centrifuging	after centrifuging at the number of revolutions per minute		
			5000	12,000	25,000
17% Orobis-2112a	400	100	100	-	100
18% Monto-702	800	100	100	100	2
13% B-370 + 4.2% PMS	900	100	70	53	2
The same after treatment by ultrasonics	600	100	-	-	47

From Table 16 one can see also that the additive Monto-702 will form in the oil a monodispersed colloidal system, and the composition of additives B-370 and PMS will form a polydisperse system: the composition partially separated out of the solution already in centrifuging at a rate of 5000 r/min, even to a greater degree at 12,000 r/min and completely settled out at 25,000 r/min. The additive Monto-702 completely settled out in centrifuging at a rate of 25,000 r/min and at lower speeds did not separate at all.

Deposits which separated from solutions during centrifuging at a rate of 25,000 r/min were investigated on an electron microscope with magnifying power of 32,500 times. Figures 32 and 33 give appropriate electron microscopic photographs which were obtained with a magnifying power of 100,000 times.

It is clear that the additive Monto-702 consists of separate particles, and the composition of additives - from aggregates of particles.

Apparently, aggregates of particles of the composition of additives can be dispersed without impairment of their effectiveness, for example, with the help of ultrasonics, inasmuch as the interaction of the latter does not change the electrical conductivity of the solutions, as we have repeatedly established. With the help of

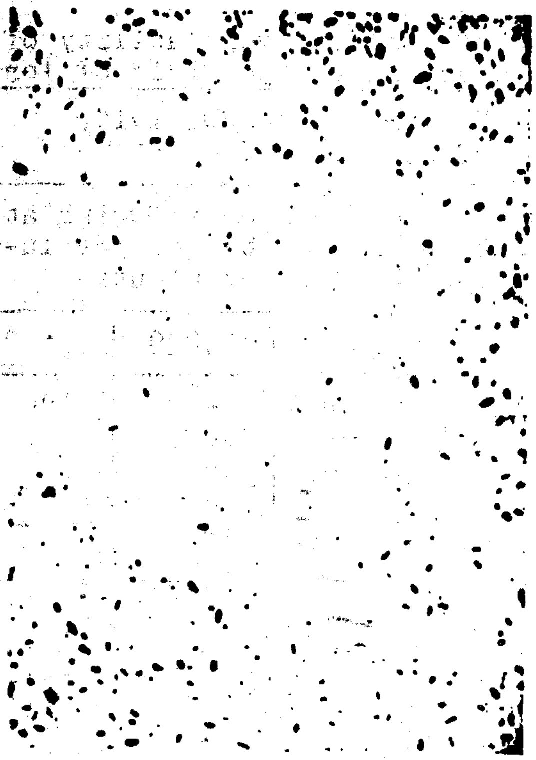

Fig. 32. Electron microscopic photograph of a deposit of additive Monto-702.

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Fig. 33. Electron microscopic photograph of a deposit of a composition of additives VNII NP-370 + + PMS.

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the ultrasonic generator [UZG-1.5] (УЗГ-1.5) with a power of 1 kW and frequency of 23 kHz, the solution of the composition of additives B-370 + PMS was treated by ultrasonics for 10 minutes. As can be seen from Table 16, after treatment by ultrasonics the stability of the solution is considerably increased: in centrifuging at a rate of 25,000 r/min approximately 50% of the additive is preserved in the solution. From Table 16 one can also see that treatment by ultrasonics of the composition of additives led to a decrease in the quantity E_0, i.e., to a decrease in the dimension of the particles. Leading to the same conclusion is a comparison of results of investigation of sorption on diatomaceous earth of the composition of additives of 13% B-370 + 4.2% PMS in oil AS-6 treated and not treated by ultrasonics. Treatment by ultrasonics increased the sorption by 18%.

Thus data of electron microscopic examinations confirmed that E_0 is characteristic of the dimension of particles of additives in oil: additives having particles of larger dimensions correspond to larger E_0 values.

It is necessary to note that solutions of additives stable in the field of force, when stability is determined by initial dimensions of particles, in certain cases can be unstable with prolonged storage; then an important role is played by the aggregate stability of the system.

Figure 34 gives mean results of a series of experiments by definition of the relative change of the saturation current in proportion to the storage of a solution of oil with additive. From Fig. 34 it is clear that the greatest stability during storage is possessed by a mixture of additives B-370 + PMS and the least, by additive Orobis-2112a.

It was determined that the effectiveness of the detergent action of solutions of additives, just as for aqueous solutions of detergent agents [88], depends on the time which passed from the

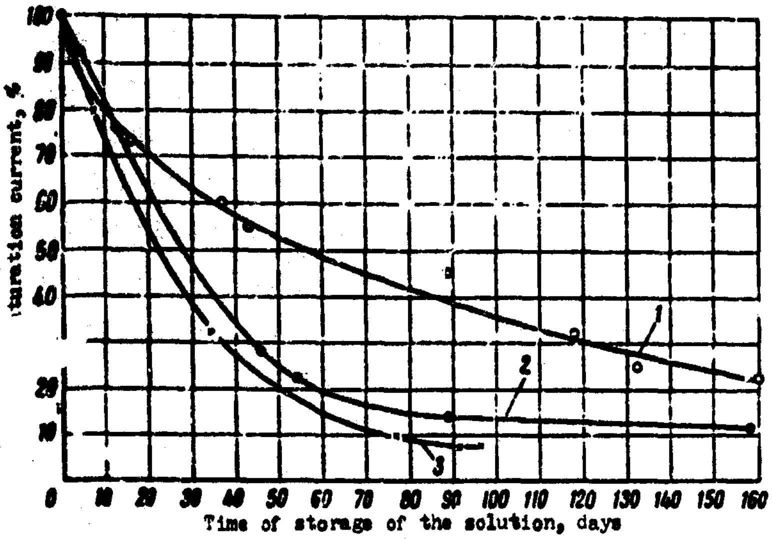

Fig. 34. Stability of solutions of additives in oil AS-6 with prolonged storage according to data of the measurement of saturation current: 1 – 4.2% PMS + 13% B-370; 2 – 18% Monto-702; 3 – 17% Orobis-2112a.

time of manufacture of the washing solution to the time of its use. The most effective detergent action under conditions of an electrical field is that of freshly manufactured solutions of additives in oils. In process of storage these solutions lose their detergent effectiveness.

Certain Data on the Structure of Particles Formed by Detergent Additives in Oils

It was already indicated above that the effectiveness of the natural detergent action of certain additives and their compositions is connected both with the charge of colloidal particles formed by additives in oils and with dimensions of these particles whose comparative characteristic is determined by the index E_0. This index does not depend on the concentration of the additive in the same oil, as can be seen from Fig. 30.

If one were to assume that the density of particles of different additives are similar in value, the particles have a spheric form, when $I_H = 0$ the inertness of the particles is determined in the first

Table 17. Indices of specific volume charges of particles of different additives in oil AS-6.

Additive	E_0	K	q	Additive	E_0	K	q
Monto-702	800	9.00	0.39	PMS	900	0.80	0.03
Monto-613	600	4.40	0.29	TsIATIM-339	450	0.13	0.01
Orobis-2112a	400	4.30	0.54	VNII NP-360	600	0.23	0.02
Orobis-2054	400	3.60	0.45	IP-22K	600	0.47	0.03
Orobis-218a	500	1.32	0.12	NG-104	600	0.15	0.01
B-370 + PMS	900	8.00	0.30	ASK	250	1.65	0.30
TsIATIM-339 + PMS	600	2.75	0.18	MASK	300	1.90	0.37
B-370	500	0.47	0.04				

[NG-104 = НГ-104, TsIATIM-339 = ЦИАТИМ-339]

place by their dimensions, then the index E_0 should be proportional to the area of maximum cross section of the particle of average dimension. With this the specific volume charge of the particle can be characterized by the tangent of the angle of inclination of straight line $I_H = f(E)$ (for metal equivalent concentration of additives) referred to $E^{3/2}$. Table 17 gives values of E_0, K indices (μA per 1000 V) proportional to tangents of angles of inclination of straight line $I_H = f(E)$, and indices of specific volume charges of particles $q = \frac{K}{E_0^{3/2}} \cdot 10^3$ of different additives for concentrations of them in oil $2.5 \cdot 10^{-4}$ g·eq metal/g of oil, which corresponds to 18% of additive Monto-702 or 17% of additive Orobis-2112a.

From Table 17 it is clear that the greatest specific volume charge is possessed by particles of additives Orobis-2112a and Orobis-2054, additives Monto-702 and Monto-613 and composition of additives B-370 + PMS. It is noteworthy that additives ASK and [MASK] (МАСК) whose solutions in oil have low electrical conductivity with a field strength of about 100 V/cm (during investigation with the help of instrument [MOM-4] (МОМ-4)) also have very high indices of specific volume charge. This, obviously, is connected with the fact that the indicated additives have particles of small dimensions and also with the fact that there is observed a nonlinear increase in electrical conductivity of solutions of these additives in oil with an increase in electric field strength, as can be seen from

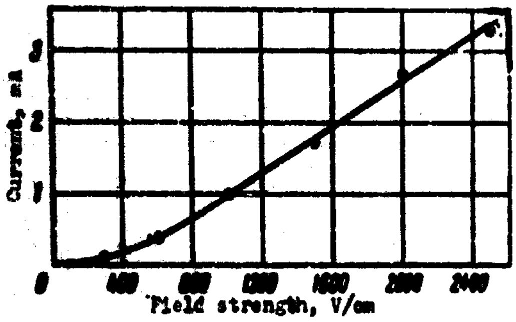

Fig. 35. Dependence of electrical conductivity of a solution of additive of 16% ASK in oil AS-6 on the electric field strength.

Fig. 35, on which data for the additive ASK are given.

Figure 36 gives the dependence of electrical conductivity (at 2500 V/cm) of solutions of additives ASK, MASK, and Monto-702 from the concentration of these additives in oil AS-6. From Fig. 36 it is clear that with small concentrations the electrical conductivities of all additives are close, and with maximum concentration the electrical conductivity of the solution of the additive Monto-702 is much more than for solutions of additives ASK and MASK. If one were to consider that indices of the specific volume charge (see Table 17) were determined for maximum equivalent concentrations of additives, then, obviously, with small concentrations this index for additives ASK and MASK should be considerably higher than that of additive Monto-702. This, in all probability, can explain the high effectiveness of additives ASK and MASK introduced in small concentrations with washing of deposits of carbon black under conditions of an electrical field (see Table 14) and also with blocking by them of the formation of deposits of carbon black on the electrodes.

Thus according to the given data one can assume that those additives which possess high detergent effectiveness in laboratory conditions and good operational properties will form, as a rule, with dissolution in oils of particles with a high index of specific volume charge, i.e., this index characterizes the effectiveness of natural detergent action of additives to motor oils.

As was shown above, in certain cases a sharp increase in

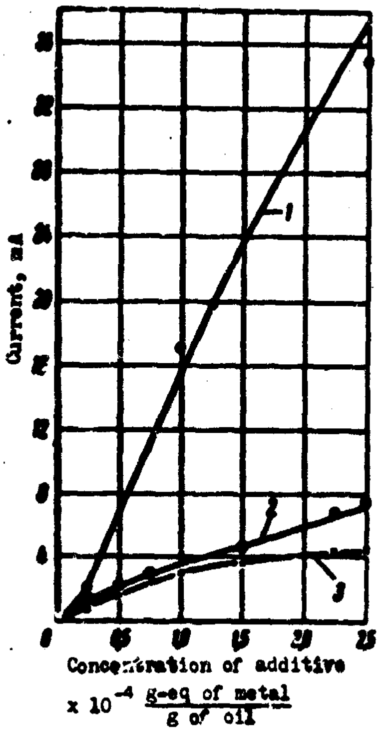

Fig. 36. Dependence of electrical conductivity of solutions of additives Monto-702 (1), ASK (2), and MASK (3) on the concentration of them in oil AS-6 with an electric field strength of 2500 V/cm.

electrical conductivity of solutions of additives in oils and, consequently, also in specific volume charge of particles of these additives can be attained because of the effect of synergism during mixing of certain types of additives whose particles separately have a low value of specific volume charge. The greatest effect was obtained with mixing of a sulfonate additive PMS and alkylphenolate additive of formaldehyde condensation VNII NP-370. As can be seen from Table 17, with the mixing of these additives the index of specific volume charge is increased by approximately one order of magnitude.

In order to study the cause of formation of particles with such high charge and to study the structure of these particles, there were conducted experiments to check the change in electrical conductivity of the solution of sulfonate additive PMS of definite concentration with an additive to it of different quantities of alkylphenolate additive VNII NP-370. In these experiments it was also clarified how the electrical conductivity of the solution of additive B-370 depends on quantity of additive PMS added to this solution. Figure 37 gives results of these experiments. It is clear that there are three rectilinear sections reflecting the different rate of growth of the electrical conductivity. The greatest growth rate of the electrical conductivity is on the second section prior to concentration of the second introduced component, which is equivalent to the initial concentration of the first component. With further increase in concentration of the second component the rate of growth of the electrical conductivity sharply decreases.

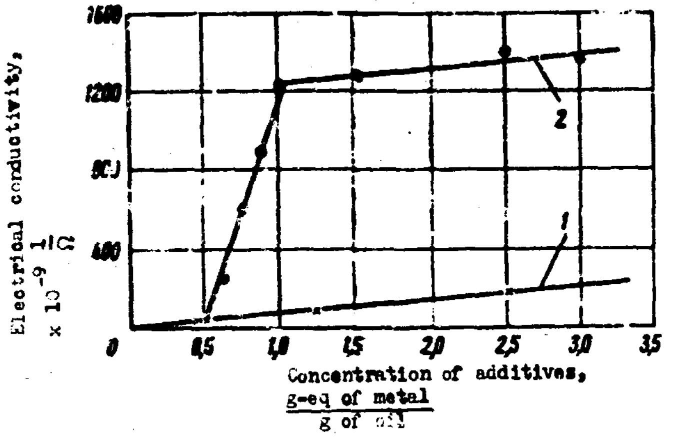

Fig. 37. Dependence of electrical conductivity of a solution of sulfonate additive PMS in oil AS-6 on the quantity of added alkylphenolate additive VNII NP-370: 1 – PMS; 2 – PMS + B-370.

From these data the conclusion can be made that for obtaining composition of additives B-370 and PMS forming in the oil particles with greatest charge and, consequently, with the best natural detergent properties, it is expedient to mix the components in concentrations equivalent in metal.

To investigate the structure of particles formed in oils by additives B-370, PMS, and their compositions, the mentioned additives labeled by isotopes Ca^{45} are synthesized. The shift in labeled additives from the lower layer of oil with an additive in the upper layer of oil without an additive, according to the diagram shown in Fig. 20, was studied. As can be seen from Figs. 38 and 39, on which there are shown results of experiments on oil with the labeled additive B-370 there is a sharp increase in radioactivity of the upper electrode with application to it of voltages +2500 and -2500 V. With this the current intensity of the circuit synchronously increased. Such a shift in the labeled metal of an additive to the positively and negatively charged upper electrode with a synchronous increase in the current indicates the complex character of cation and anionic

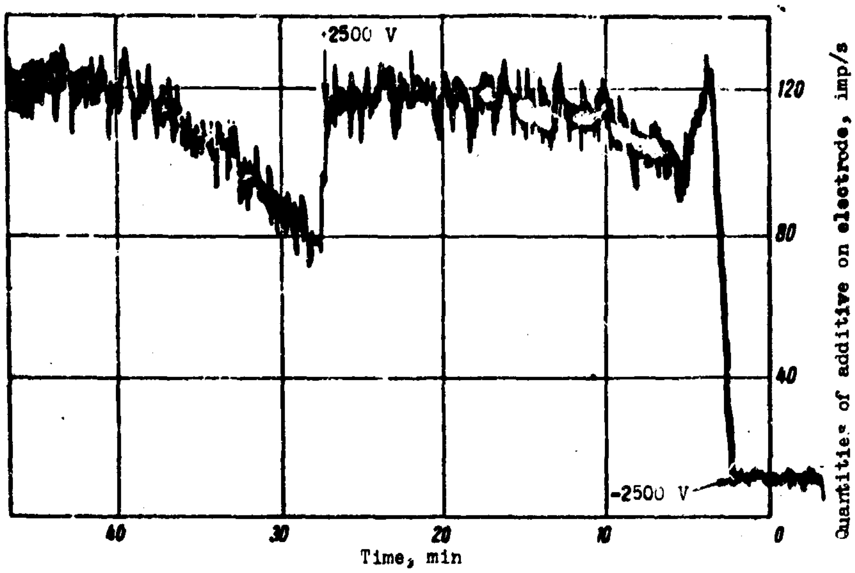

Fig. 38. Automatically recorded diagram reflecting the behavior of labeled additive B-370 with application to the upper electrode of first -2500 V and then +2500 V.

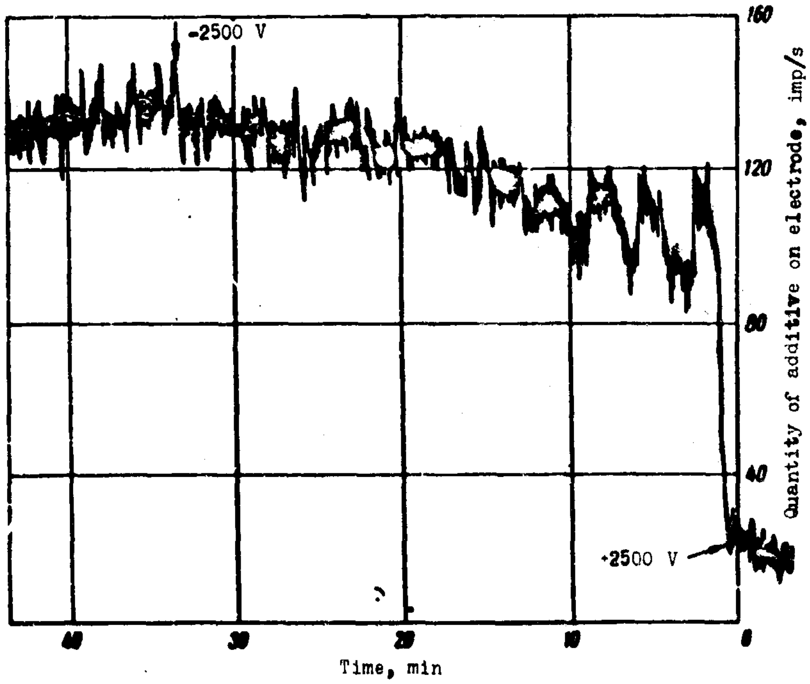

Fig. 39. Automatically recorded diagram reflecting behavior of labeled additive B-370 with application to the upper electrode of first +2500 V and then -2500 V.

charge carriers, formed by the additive B-370 in oil: the metal is contained both in cation and in anionic particles.

The multiple repetition of experiments with the labeled additive B-370 also showed (see Figs. 38 and 39) that the duration of accretion of radioactivity with time with the application to the upper electrode of +2500 V was greater (70 s) than with application of -2500 V (45 s), which indicates the greater mobility of cation particles as compared to anionic. The same conclusion is drawn for the consideration of the form of curves of the change in radioactivity with time during a change in sign of the charge of the upper electrode: when switching from minus to plus (see Fig. 38) the radioactivity with subsequent slow accretion sharply decreases; such an effect is connected with the fact that with the indicated switching more mobile cations rapidly depart from the space near the electrode, and less mobile anions gradually occupy their place. With a change in sign of the charge of the upper electrode from positive to negative (see Fig. 39) a sharp change in radioactivity is absent, and there is observed a gradual increase in radioactivity, which furthermore is connected with different mobility of cation and anionic particles of the additive.

Oil containing 8.5% labeled additive B-370 in a mixture with different concentrations of the additive PMS was investigated. Figures 40 and 41 give, for example, results of investigations of compositions containing 1.68 and 8.4% of the additive PMS. The obtained diagrams permitted drawing the conclusion that the duration of accretion of radioactivity with time is increased with an application to the upper electrode of both +2500 V and -2500 V with a growth in concentration of additive PMS in the mixture, which indicates a decrease in mobility of cation and anionic particles containing Ca^{45} of additive B-370.

Investigations of labeled additive PMS and its mixtures with different concentrations of additive B-370 also showed the complex character of cation and anionic particles, charge carriers, formed

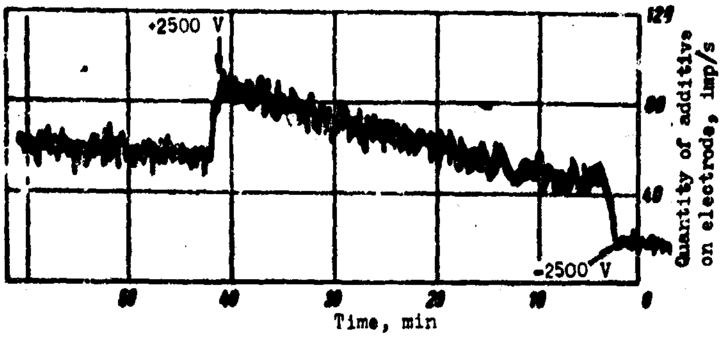

Fig. 40. Automatically recorded diagram reflecting the behavior of labeled additive B-370 in a mixture with 1.68% of additive PMS under conditions of action of an electrical field.

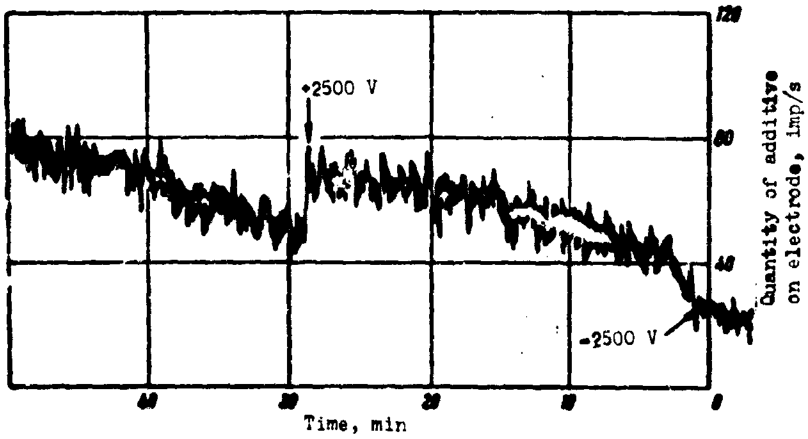

Fig. 41. Automatically recorded diagram reflecting the behavior of labeled additive B-370 in a mixture with 8.4% of additive PMS under conditions of the action of an electrical field.

in the oil by additive PMS and its mixtures with additive B-370: Ca^{45} of additive PMS was contained in cation and in anionic particles. These investigations also showed the great mobility of cation particles as compared to anionic.

Footnotes

[1] Recently Anderson and Fowkes [85] in the United States also started to investigate the behavior of carbon black in the electric field to study the mechanism of action of dispersive additives to oils.

[2] The indicated percent of additives provided radioactivity of the oil necessary for registration.

[3] Such a determination of the stability of solutions of detergent additives in oils is simpler than the earlier radiometric method developed by us, which was founded on the measurement of radiation of labeled additives [89, 90] and is used abroad [91].

CHAPTER 4

INVESTIGATION OF THE MECHANISM OF ANTICORROSIVE ACTION OF ADDITIVES TO OILS

Study of Properties of Films Formed by Additives on Metals

It is known that corrosional destruction of bearings of nonferrous antifriction alloys in the process of the operation of internal combustion engines is caused in the first place by products of oxidation of oils - high-molecular acids, low-molecular organic and inorganic acids - products of fuel combustion, and also certain sulfurous compounds [92].

Corrosion of the most widespread antifriction alloy - lead bronze - is connected mainly with the washing out of the lead component [92, 93].

Destruction of nonferrous antifriction alloys under the action of high-molecular organic acids occurs basically as a result of the chemical corrosion occurring in general according to the following scheme: in the first period of the influence of the medium on metal there occurs a chemical compound of atoms of the medium with atoms of the metal and formation of the first monomolecular layer of the chemical compound [94]. However, this monomolecular layer is not a fully sufficient barrier for further interaction.

As a result of bilateral diffusion processes both on the side of the metal and on the side of the medium there is observed further raising of layers of the chemical compound, i.e., essentially there will be formed a protective film on the surface of the metal, and the corrosional process is considerably delayed.

Investigations of the mechanism of action of anticorrosive additives to motor oils are the subject of a number of works in the Soviet Union and abroad. Almost all researchers are divided in their opinion about the fact that the mechanism of action of anticorrosive additives leads to the formation by basic components of additives of protective films on the surface of metals [92, 95-101].

In literature it is indicated [102] that the action of anticorrosive additives is connected with the occurrence of a number of processes both in volume of oil and on the surface of metal bordering with the oil. Such processes can include deceleration of the reaction of oxidation of oil with the influence on the process of formation and disintegration of peroxides (primary products of autooxidation of hydrocarbons), the passivation of metallic surfaces catalyzing in the absence of additives the process of oxidation of oil, and the formation on the surface of the metal of protective films of sulfur or phosphorus, which are present in additives in the form of different compounds. The last process is the least studied with respect to conditions of the formation of protective films and from the point of view of their chemical nature [98, 102].

In literature it is indicated [92] that as anticorrosive additives to motor oils it is possible to use only such compounds which are able to interact chemically with metals and to form on their surface sufficiently durable protective coverings able to be restored with mechanical abrasion or during the action on them of acid products.

In later works [103-114], devoted to the study of the mechanism of action of the examined additives, with the help of the method of labeled atoms it is shown that sulfur-organic and phosphor-organic compounds will form films on surfaces of different metals. Examined also is the influence of different factors (time of interaction of additive with metal, character of metal, temperature of oil, composition and concentration of additive on kinetics of the formation of the film [103-114].

In carrying out these investigations the distinction in temperature borders of the most effective interaction of sulfur and phosphorus with metals is established [103-112]. The same distinction with respect to sulfur and phosphorus is set with the investigation of counterseizing additives [115-117].

However, observation of kinetics of the formation by additives of films on surfaces of metals without simultaneous observation of destruction of the latter did not permit estimating the protective effectiveness of the forming films. The solving such a problem proved to be possible on the basis of the application of our developed [103, 105, 112, 114] radiochemical method of the investigation of corrosion of metals under the action of oils.

Investigations were conducted on the Pinkevich-oil bath apparatus, in which there are set 8 glass test tubes with oils to be tested. With the help of a crankgear into each of the test tubes there were periodically put metallic disks 15 mm in diameter and 4.2 mm thick; there was used a test tube with a diameter of 20 mm and length 210 mm, and the test tube was filled with 17 g of oil [105, 106]. The indicated dimensions of test tubes and quantity of oil are accepted for preservation of the relationship between the duration of stay of plates in the oil and air specified during operation of the apparatus according to the All Union Government Standard 5162-49.

To investigate the corrosion there were used radioactive metallic plates, activated either by irradiation by neutrons in the channel of a nuclear reactor with the obtaining of radioactive isotopes possessing γ-radiation (Fe^{59} in steel and cast iron plates), or by introduction of γ-active isotope into molten metal with the casting of disks. The irradiation of lead and copper plates in the flow of neutrons does not provide obtaining in their composition radioactive isotopes with half-lives and radiations suitable for corrosion studies [105, 106]. In connection with this we developed the method of obtaining radioactive nonferrous metals and alloys by means of the introduction of a radioactive isotope with a useful half-life for purposes of investigation and energy of γ-radiation.

There were activated lead samples for the study of corrosion, introducing into lead the radioactive isotope Sb^{124} with a half-life of 60 days, which possesses γ-radiation with maximum energy of more than 2 MeV. The lead was melted in a crucible in muffle furnace and overheated to a temperature of 700°C. After the indicated temperature was established into the melt small piece of lead containing a hinge of radioactive antimony were introduced. Before this radioactive antimony in the form of metallic powder was injected into a hole drilled in this piece of lead, and the hole tightly closed by a lead plug.

The magnitude of the hinge of antimony was selected with such calculation so as to obtain after melt radioactive lead with the desirable specific activity (0.2-0.5 μCi/g) with a maximum content of antimony in lead as a mechanical impurity of not more 0.001%. After melting of a piece of lead containing antimony, the melt in the furnace was thoroughly mixed for equal distribution of radioactive antimony in the lead. The crucible was removed from the furnace, and radioactive lead was poured into the copper tube with internal diameter of 15 mm. The thus obtained billet was set in a chuck of a lathe on which there were cut disks 5 mm in thickness, and one of surfaces of every disk was treated by a face cutter to standard cleanness. Around cylindrical surface there was made a loop of thin wire whose ends were twisted in the form of a bug for suspending in the Pinkevich apparatus. The prepared sample was insulated three times by the application of a thin layer of glue [BF-2] (БФ-2) on all copper surfaces, the wire and inoperative surface of the lead in such a manner that during the investigation of corrosion only one end flat lead surface of the disk 15 mm operated.

Prior to the carrying out of experiments the prepared disks were stored in an exsiccator. With each melt a check was conducted on the equal distribution of radioactive antimony in a mass of lead by laminar measurement of radioactivity [105]. Radioactive copper disks activated by Ag^{110} were prepared similarly.

During operation of the Pinkevich apparatus due to corrosion of the disks the radioactive metal converted to oil and therefore the radioactivity of the tested oils was changed. The test tubes with oil were periodically removed from the oil bath and were installed inside the unit of six gamma-ray counters placed in the lead chamber for measurement of radioactivity of oil [118, 119]. The duration of measurement of radioactivity of every sample provided obtaining of data with a relative mean square error of ±3%. Conversion data of radiometric measurements into a weight quantity of metal, which passed over as a result of corrosion in the oil, was carried out with the help of standardization [118, 120].

In connection with the fact that by the developed method the corrosion of lead is observed by radiation of Sb^{124} passed over to the oil, it was checked how identically washing out of lead and antimony occurs under the corroding influence of oil. For this purpose there was conducted a series of experiments during which the corrosion of lead disks operating in oil MT-16 was determined both radiometrically and by weighting of the disks. Both methods showed identical results. In connection with the fact that with weighting of the disk there is fixed the loss of lead due to corrosion and overweight of the disk because of the presence on the surface of products of interaction of lead with oil, weighting gives less accurate values of magnitudes of corrosion.

To investigate the formation of protective films there were synthesized anticorrosive additives labeled by radioactive isotopes of basic components (S^{35}, P^{32}, C^{14}). Oils containing labeled additives were tested in the Pinkevich apparatus with nonradioactive disks. After definite time intervals the disks were removed from the apparatus, washed in gasoline and benzene, dried and placed in a lead chamber under an end-window counter. Between the counter and disk an aluminum filter with round hole of 1 cm^2 was placed. The radioactivity on the surface of disks with a duration providing a relative mean square error of ±3% was measured.

To convert data of radiometric measurements into weight indices, taking into account disintegration of the radio isotope, standard solutions were prepared which were applied in the form drops on the surface of the control disks. After evaporation of the liquid phase the radioactivity on the surface of the disks were periodically measured, and was compared with the activity of the working disks [105, 106]. Sensitivity of the quantitative determination with specific activities of the used isotopes amounted to 10^{-7}-10^{-8}g.

For example, Figs. 42 and 43 give results of investigations of the kinetics of the formation of protective film on the lead by the additive barium disulfide alkylphenolate (3% in oil MT-16), labeled by S^{35}, and corrosion of lead at temperatures of the oil of 140° and 170°C. From Figs. 42 and 43 it is evident that the kinetics of corrosion of lead is connected with the kinetics of the formation of the protective film on lead by a labeled additive and destruction of the film: the intensity of the corrosion of lead is noticeably increased after the quantity of protective film starts to decrease, and corrosion is accelerated after full disappearance of the film.

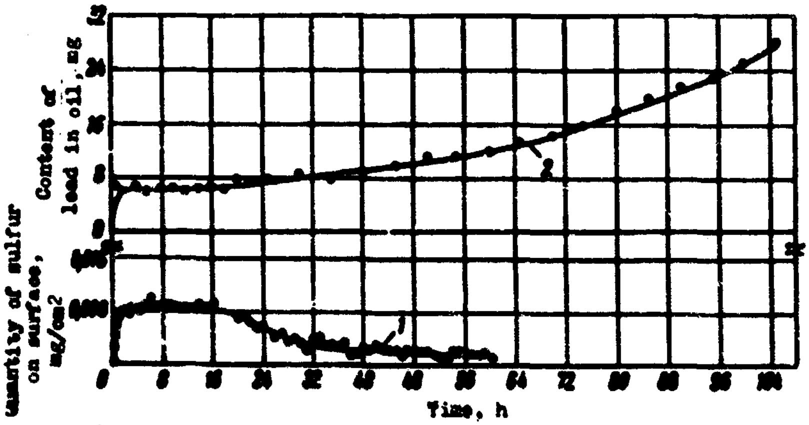

Fig. 42. Kinetics of the formation of a protective film on lead by the additive barium disulfide alkyphenolate (3% in oil MT-16) and kinetics of the corrosion of lead at a temperature of oil of 140°C: 1 – formation of protective film; 2 – corrosion of lead.

A comparison of experimental data given in Figs. 42 and 43 shows that with a temperature rise the quantity of the protective film is increased; it will be formed faster but is preserved on the surface of the metal for a much less prolonged time.

Thus there is obtained direct experimental proof of the formation of protective films on the surface of metal as a basic mechanism of action of anticorrosive additives to mineral oils.

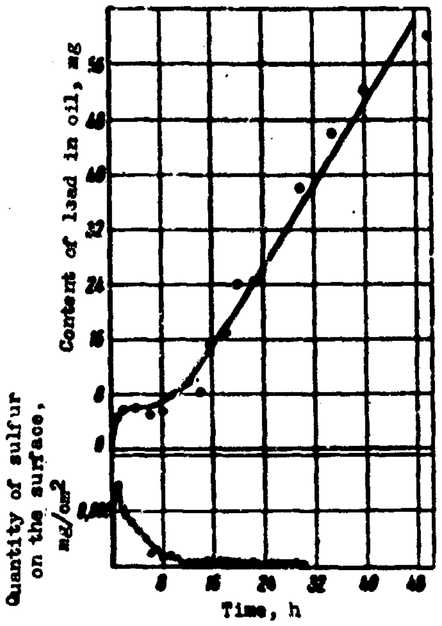

Fig. 43. Kinetics of formation of protective film on lead by the additive barium disulfide alkylphenolate (3% in oil MT-16) and kinetics of corrosion of lead at a temperature of oil of 170°C.

It is necessary to pay special attention to kinetics of the formation of protective films. Apparently there exist two stages of formation of the protective film on the metal surface: the first stage is a direct interaction of the additive with metal with the formation of a basic protective layer of film; the second stage is the raising of the layers of the film, but these layers, obviously, do not create an additional anticorrosive effect. Such a point of view is confirmed in examining the character of curves of the film formation and corrosion shown in Fig. 44 (oil MT-16 + 3% sulphurized alkyl phenol labeled by isotope S^{35}) on which there are especially clearly seen two stages of growth of the quantity of film, and it is also clear that the intensity of corrosion noticeably drops in the first stage of film formation and does not change in the second stage.

The process of departure of the film from the surface, as one can see from obtained results of the investigation, also occurs in two stages: the first stage differs by a gradual decrease in quantity of film on the surface with a simultaneous increase in intensity of corrosion, and the second stage is characterized by full disappearance of protective film from the surface, where simultaneously with this the intensity of corrosion is again noticeably increased.

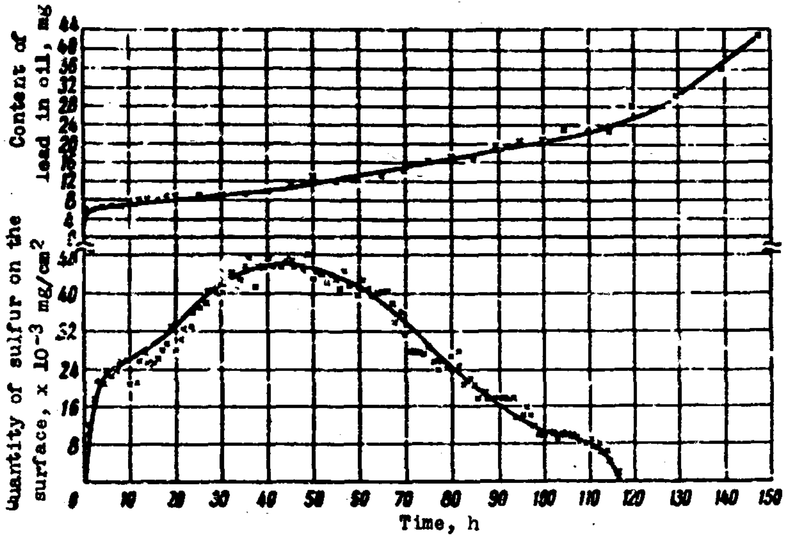

Fig. 44. Kinetics of the formation of protective film on lead by sulphurized alkyl phenol labeled S^{35} (3% in oil MT-16), and the kinetics of the corrosion of lead at a temperature of oil of 140°C.

It seems to us that the process of disappearance of film from the surface and the increase in intensity of corrosion of metal connected with it can be explained in the following way: according to oxidation of oil in the process of its operation there occurs an accumulation of appropriate acid products (acids, phenol, etc.) and a formation of lead soaps - products of the interaction of fatty acids with metal. The latter is observed under conditions of intense film formation both in its first and second stage, which is clear from the growth of corrosion in the period of the second stage of formation of the protective film.

Accumulating in the oil, acid products and soaps are able to destroy and to wash off the protective film. Apparently, during the first two stages of the formation of the protective film the process of the accumulation of film on the surface prevails over the process of its washing and destruction. Subsequently the process of washing and destruction of the film, connected with the intense accumulation of soaps and acid products in oil, starts to predominate over the process of formation of the film in consequency of which the departure of the film from the surface is observed [105-108].

Experiments were conducted for a more detailed investigation of the causes of departure from the surface of the metal of protective film created by the anticorrosive additive [121-123]. Eight lead plates operated in the Pinkevich apparatus 12 hours on oil MT-16 with labeled S^{35} by additive barium disulfide alkylphenolate at a temperature of oil of 140°C. The quantity of the forming film and kinetics of its formation on all plates were absolutely identical and analogous to that established earlier (see Fig. 42). The plates with the film formed on them were placed in different oils: MT-16 with 3% barium alkylphenolate, MT-16 and MK-22 in which the plates continued to operate on the Pinkevich apparatus; observation of the quantity of film on the surface of the plates continued. Results of these experiments are shown in Fig. 45a, b and c.

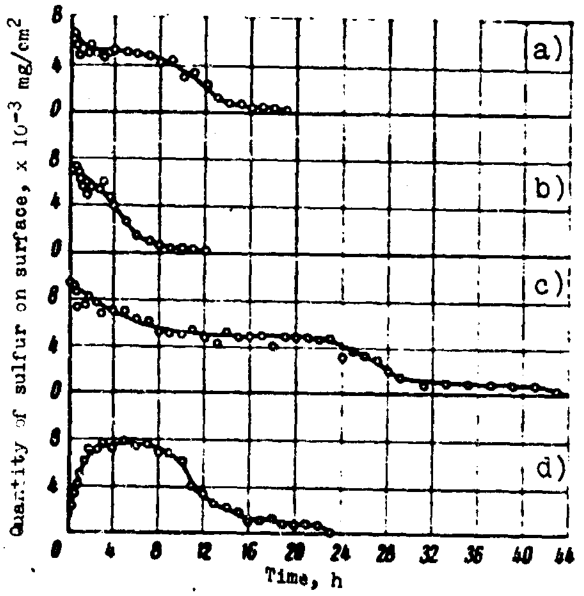

Fig. 45. Kinetics of the destruction of the protective film formed on the surface of lead by the additive barium disulfide alkylphenolate under the action of acid products and soaps. Temperature of the oil - 140°C. a) MT-16 + 3% barium alkylphenolate, working plate; b) MT-16 working plate; c) MK-22 working plate; d) spent oil + + 3% barium disulfide alkylphenolate, new plate.

As can be seen from Fig. 45, the oil containing the detergent additive, barium alkylphenolate, gradually washed off the protective film formed earlier on the surface of lead by the labeled additive barium disulfide alkylphenolate. Furthermore, it is clear that with a different content in oil of acid products (acid number of oil MT-16 - 0.35 mg KOH, and MK-22 - 0.10 mg KOH) and different rate of their accumulation in the process of oxidation, destruction of the protective film occurs unequally: in oil MT-16 the film is washed off in 12 h and in oil MK-22 – in 46 hours.

Such a result convincingly shows that the protective film forming with work of the oil with anticorrosive additive is not maintained constant on the surface of metal prior to the moment when it starts to be destroyed and there occur two competing processes: formation of film by the additive and destruction and washing of it by acid products and soaps, and the second process is even more strengthened with the growth in oil of a quantity of acid products and soaps which can destroy the additive.

The expressed position is well confirmed with a comparison of experiments conducted at temperatures of oil of 140° and 170°C (see Figs. 42 and 43): with an increase in temperature there is accelerated not only the process of formation of the film but also the process of its destruction, which is connected with a more intense flow of the oxidation of oil, accumulation in it of soaps and phenolates, and also the very probable destruction of the additive in oxidized oil.

From what has been said it follows that to provide effective anticorrosive action the additive should possibly be able for a longer period continuously to restore on the surface of the metal the destroyed and washed protective film, i.e., should wear as slow as possible.

The effect of the "wearing capacity" is additionally checked by us with the help of the following experiments [105-107]. In oil MT-16 with the additive barium disulfide alkylphenolate labeled by S^{35} operating at 140°C in the Pinkevich apparatus for 62 hours (the duration set earlier of the formation of film by the indicated additive to its full departure from the surface of the metal), there was inserted a new lead plate and for 17 hours the formation on its surface of protective film was investigated. However, during this period no film was formed on the surface. Further to the same oil was added 10% fresh oil with an additive (near 0.3% additive), and the experiment continued 13 hours more. Film was not revealed. Only with the replacement of half of the oil by fresh oil, (i.e., with the introduction of 1.5% fresh additive) was there registered a formation of protective film in a quantity five times smaller than that observed in experiments on fresh oil with 3% additive where already after 3 hours work the film vanished from the surface.

An experiment is conducted during which into oil MT-16 with labeled additive barium disulfide alkylphenolate working at 140°C for 62 hours there was introduced 3% fresh additive, and the plate operated in apparatus for 25 hours more. Results of this experiment are shown on Fig. 45d from which it is clear that the film was formed in that same quantity and approximately at the same rate as that in experiments with fresh oil with the indicated labeled additive. However, departure of the film from the surface of lead began already after 10 hours and its full disappearance occurred after 23 hours instead of 18 and 62 hours respectively on fresh oil with an additive, i.e., the period of wear capacity of the additive was sharply reduced, which is connected with the high content of acid products and soaps accumulated in the working oil before the time of introduction into it of fresh additive.

For obtaining experimental proof of the conventional point of sight on the ability of the additive to restore the protective film during its mechanical destruction (as a result of the processes of friction and wear occurring in main and connecting rod bearings of an engine) there was conducted an experiment on oil MT-16 with labeled additive barium disulfide alkylphenolate at 140°C. The kinetics of the formation of protective film on the surface of the lead plate was investigated during operation of the Pinkevich apparatus for 62 hours. After 22 hours the film formed was completely removed from the surface of the plate by filter paper, after which the plate continued to operate. Results of the experiment are shown on Fig. 46 from which it is clear that during the 23rd hour of operation of the oil on the plate there was formed again a protective film in quantity analogous to that which was formed during the first hour of operation of plate. During further 5 hours the film completely rose to the same quantity as it was prior to abrasion of film. Further process of its existence on the surface and departure from the latter is analogous in character and coincides in period (61 hours) with behavior of the film in the experiments where there was no abrasion of it. Repetition of this experiment three times gave completely coinciding results.

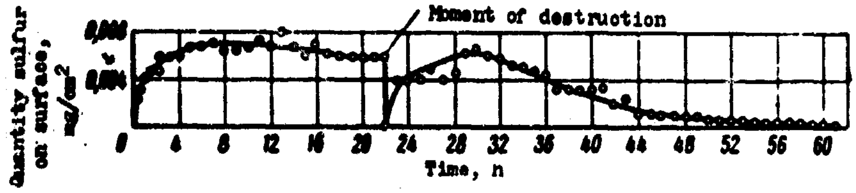

Fig. 46. Kinetics of restoration of protective film formed on the surface of lead of 3% additive barium disulfide alkylphenolate to oil MT-16 after mechanical destruction of the film. Temperature of oil, 140°C.

Thus it is experimentally shown that an anticorrosive additive restores on the surface of the metal mechanically a destroyed protective film if destruction of the film occurred before the additive was worn.

Influence of Organic Acids on Kinetics of Formation of Protective Films by Sulfur-Containing Additives

In connection with the set determining influence of acid products and soaps forming during oxidation of the oil, on the process of destruction of protective film and the process of corrosion connected with it there is conducted an investigation of the kinetics of formation and destruction of protective film and corrosion of lead under the action of organic acids specially introduced into the oil [121].

In oil MT-16 containing 3% additive of barium disulfide alkylphenolate labeled by S^{35}, there were added different quantities (from 0.1 to 7.0%) oleinic, palmitic or naphthenic acids. Investigations were conducted in the Pinkevich apparatus at a temperature of oil of 140°C.

Figures 47 and 48 give results of these experiments. Figure 47 shows, for example, typical results of the experiment with designations accepted further. Figure 48 shows generalized results of experiments obtained with the introduction of naphthenic acids.

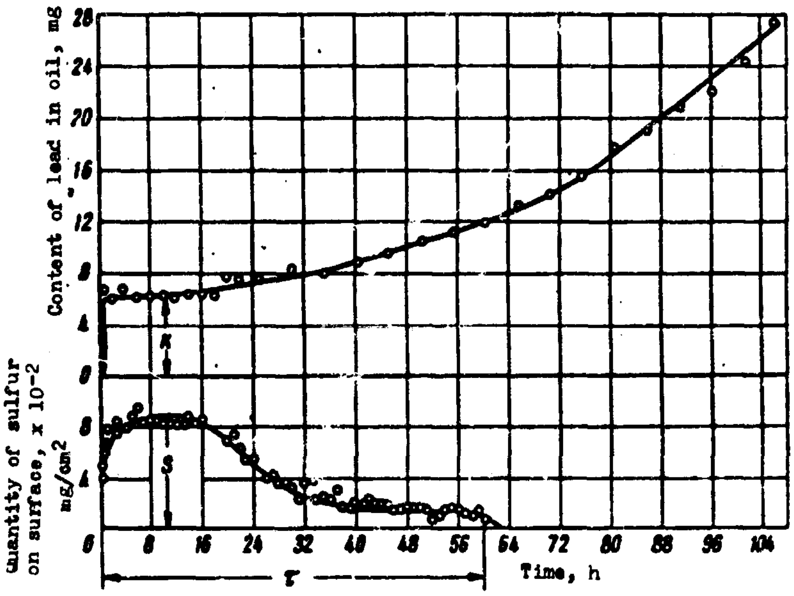

Fig. 47. Kinetics of the formation of protective film on lead by the additive barium disulfide alkylphenolate (3% in oils MT-16) and the kinetics of the corrosion of lead at a temperature of oil of 140°C.

Plotted along the axis of the abscissas is the quantity of acid (in %) introduced into the oil. Plotted along the axis of the ordinates are (see Fig. 47): the maximum quantity of film S, determined by an appropriate curve of kinetics of the formation of the film; 2) duration of the existence of film on the surface of lead τ under those same conditions, which was determined by the same kinetic curves (see Fig. 47); 3) magnitude of corrosion K under those same conditions, which was determined by curves of kinetics of corrosion during the time corresponding to the maximum quantity of film.

From the curves shown in Fig. 48 it follows that with an increase in quantity of introduced acids the duration of the existence of the film sharply decreases and then slowly increases. The maximum quantity of the forming film and the corresponding corrosion of lead after an insignificant decrease increase rather rapidly. All curves have minima with the same quantity of acids introduced into the oil. An analogous character of the curves is obtained in experiments with oleinic and palmitic acids. Such minima on curves show that with introduction into the oil with an anticorrosive additive of small quantities of organic acids there is improved the protective effectiveness of the film, in consequence of which the corrosion of lead decreases but the time of existence of film on its surface is reduced.

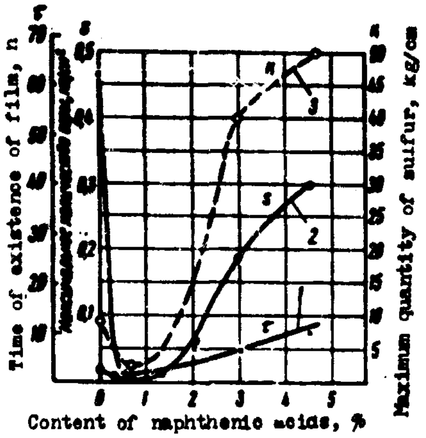

Fig. 48. Influence of naphthenic acids on the protective effectiveness of films formed by barium disulfide alkylphenolate on lead: 1 – time of existence of film τ; 2 – maximum quantity of film S on the surface of lead; 3 – corrosion of lead K with maximum quantity of film from its surface.

Apparently, such an effect is connected with the polishing action of the investigated acids with respect to the surface of metal (which was observed for plates in these experiments) during simultaneous destroying action of these acids on the anticorrosive additive in a volume of oil. The latter is confirmed by shape of the curves to the right of the minimum when, in spite of the increase in quantity of film and time of its existence on the lead surface, its corrosion is increased sharply. This, probably, is connected with the transition occurring during destruction of the additive of sulfur into a more reactive-capable state in which it does not possess anticorrosive properties, but interacting with the surface of lead, causes intense corrosional destruction of latter.

The effect of destruction of the additive by acid products in a volume of oil is clearly seen also from results of experiments shown in Fig. 49. The figure shows curves of the formation of a protective film on lead by barium disulfide alkylphenolate labeled in one case by sulfur S^{35} and in another case[1] – C^{14}, and also a corresponding curve of the corrosion of lead. These experiments were conducted on oil MT-16 with 3% of the mentioned additive and 6% of naphthenic acids at a temperature of the oil of 140°C.

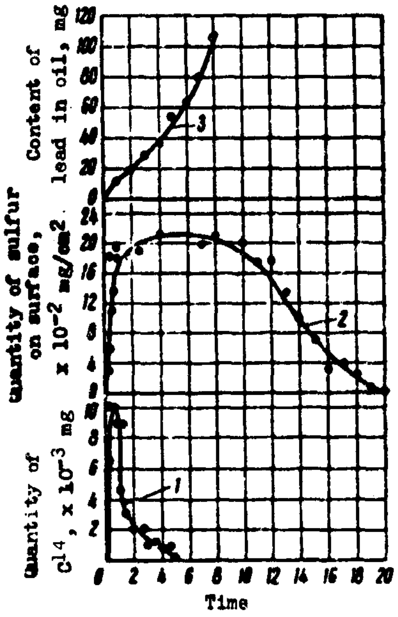

Fig. 49. Kinetics of the formation of protective films on lead by barium disulfide alkylphenolate, marked by isotopes S^{35} and C^{14}, and kinetics of the corrosion of lead. Oil MT-16 with 3% additive and 6% naphthenic acids. Temperature of oil, 140°C: 1 – film recorded by radiation of C^{14}; 2 – film recorded by radiation of S^{35}; 3 – corrosion of lead.

The growth in quantity of film recorded by S^{35} and C^{14} in the first 20 minutes indicates that in this period of time the film will be formed by molecules of the additive, apparently, with the formation of the complex compound [124]. Further movement of the curves plotted by radiation of S^{35} and C^{14} is absolutely distinguished: the quantity of film with respect to C^{14} sharply drops, and with respect to S^{35} continues to increase up to the moment (5 hours) full disappearance of the film with respect to C^{14}, after which it also starts to decrease. Accordingly after 5 hours an increase in the corrosion rate of lead is observed. The shape of the examined curves, as it seems to us, indicates after 20 minutes operation under conditions of high content of acids in oil the advancing intense destruction of the additive in the volume of oil. The subsequent decrease in the quantity of sulfur on the surface is

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[1] Synthesis of the additive by labeled isotope C^{14} was conducted on the basis of phenol containing one atom of C^{14}.

connected with corrosional destruction of the metal.

Influence of Strength of the Bond of Sulfur in a Molecule on Anticorrosive Effectiveness of the Additive

From Fig. 49 it is clear that the most effective protection of lead from corrosion was provided by an additive as long as the protective film consisted of molecules of the additive. This very significant conclusion was checked with the help of an individual sulfur organic compound [124].

The oil MT-16 received 2.8% diphelylsulfide labeled by S^{35} and C^{14}. Experiments were conducted on the Pinkevich apparatus at a temperature of oil of 140°C. Results of experiments are shown in Fig. 50. It is clear that the most effective retardation of corrosion is provided during the first 8 hours when the composition of film on the surface of lead includes both sulfurs and radicals of additive, i.e., the most effective protection is provided by film consisting of molecules of the additive.

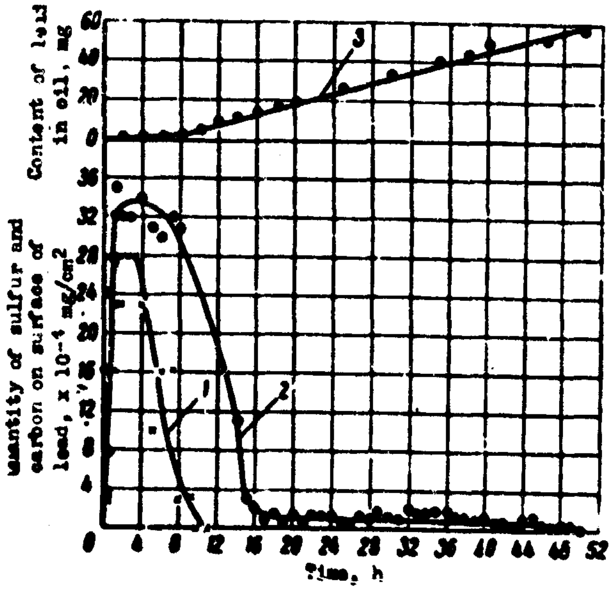

Fig. 50. Kinetics of the formation of protective films on lead by diphenyl sulfide, labeled by isotopes S^{35} (2) and C^{14} (1) and kinetics of the corrosion of lead (3). Oil MT-16 with 2.8% additive. Temperature of oil, 140°C.

Thus results of the investigations lead to the conclusion that as anticorrosive additives to motor oils most effectively lowering the corrosion of bushings it is expedient to use polar sulfur-containing compounds in molecules of which the sulfur possesses relatively more durable bonds. By this, from out point of view, the sulfur-containing compounds, most effective as anticorrosive additives, differ from the sulfur-containing compounds which are promising for the application as counterseizing additives easily splitting the sulfur [117].

The conclusion drawn is well confirmed by results of investigations of anticorrosive properties of a number of individual sulfurous compounds conducted by us [121, 122, 124] and also other authors [125].

Figures 51 and 52 show the results obtained by us of the investigation of anticorrosive properties didecylsulfide didecyl disulfide and decylmercaptan, labeled by S^{35} and introduced into oil MT-16 in various quantities from calculation of the identical content of sulfur in oil. As can be seen from Fig. 51, the sulfide in whose molecule sulfur possesses a more durable bond than that in the molecule of disulfide will form a protective film which is retained considerably longer on the surface of lead and, consequently, provides considerably lesser corrosion of the lead one than that of disulfide. From Fig. 52, on which results are given of the radiometric determination of corrosion of lead for an identical time (30 hours) of operation of the Pinkevich apparatus at various temperatures of the oil, it follows that didecylsulfide is thermally stable and does not lose anticorrosive effectiveness with a temperature rise of the oil, whereas both the didecyldisulfide, and decylmercaptan are unstable, and didecyl disulfide even increases corrosional aggressiveness of oil MT-16 in the whole range of investigated temperatures.

From the same figure it follows that the estimate of anticorrosive effectiveness of additives only at any temperature is insufficient in connection with the fact that thermally unstable (from the point of view of destruction of the molecules) additives possess very different anticorrosive effectiveness at different temperatures.

Thus from Table 18, in which there are given certain results of investigations of anticorrosive effectiveness of different individual sulfur-containing compounds, it is clear that approximately identical anticorrosive effectiveness of diphenyl sulfide and diphenyl disulfide at 140°C, noted by S. E. Kreyn and G. S. Tarmanyan [125], coinciding with our data at that same temperature, sharply changes with an increase in temperature: the diphenolsulfide preserves its anticorrosive effectiveness, but with diphenyl disulfide it considerably worsens.

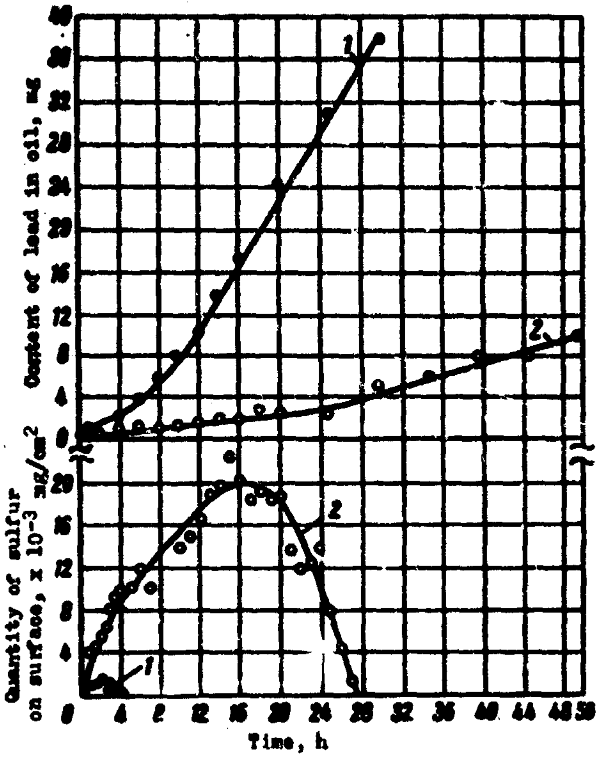

Fig. 51. Kinetics of the formation of protective films on lead by didecyl sulfide and didecyldisulfide labeled S^{35} and kinetics of the corrosion of lead. Oil MT-16. Temperature of oil, 170°C: 1 – didecyl disulfide; 2 – didecyl sulfide

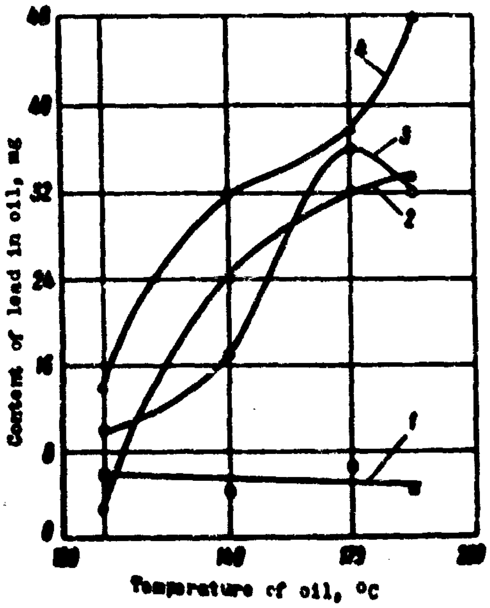

Fig. 52. Dependence of corrosion of lead on temperature of oil and the type of sulfurous compound introduced into the oil. Results are obtained on the Pinkevich apparatus during a test of the oils; 1 – MT-16 + 1.2% didecylsulfide; 2 – MT-16 + + 0.6% decyl mercaptan; 3 – MT-16; 4 – MT-16 + 0.6% didecyl disulfide.

Table 18. Anticorrosive effectiveness of different individual sulfurous compounds.

Sulfurous compound	Corrosion of lead at a temperature of oil		
	170°C	140°C	140°C (after data of work [125], g/m^2)
	(after our data by the radiochemical method), mg		
Didecylsulfide	6,0	5,0	—
Didecyldisulfide	38,0	32,0	—
Decylmercaptan	33,0	25,0	43,2
Didecylsulfide	30,0	28,0	15,9
Didecyldisulfide	50,0	32,0	16,0
Dioctadecyl sulfide	13,0	—	10,2
Dioctadecyl disulfide	58,0	—	—
Dinonyl sulfide	—	—	11,1
Dinonyl disulfide	—	—	16,5

From Table 18 one can see also that the sulfides provided the better anticorrosive effectiveness than did the corresponding disulfides. Apparently, one can assume that organic sulfides in molecules of which sulfur possesses more durable bonds than those in corresponding disulfides, are more promising as anticorrosive additives than the disulfides.

Influence of Salts of High-Molecular Acids on Kinetics of the Formation of Protective Films of Sulfur-Containing Additives

To checking the influence of soaps on processes of formation and destruction of protective films and corrosion of lead there were conducted experiments with the introduction into the oil of naphthenates of different metals at a temperature of oil of 140°C [121].

To oil MT-16, containing 3% barium disulfide alkylphenolate labeled by S^{35}, were added different quantities (from 0.05 to 12%) of naphthenates of cobalt, lead and copper. Figure 53 gives curves (which generalize results of these experiments) plotted analogous to curves shown in Fig. 48. Values of acid numbers shown on the axis of absicissas of Fig. 53 for oil with a different content of naphthenate of cobalt are conditional, since naphthenic salts are capable of hydrolysis even with titration by alcohol alkali. Curves on Fig. 53 reflect the total influence of salts and acids, since the used naphthenates had excess acidity. However, a comparison of results of experiments with the introduction of naphthenic acids (see Fig. 48) with the curves on Fig. 53 permits estimating the influence of salts on the examined processes. It is clear that with the introduction of a great quantity of cobalt naphthenate into the oil the maximum quantity of film on the surface of lead at first somewhat decreases and then rapidly increases. The duration of the existence of the film at first sharply decreases and then slowly increases analogous to that which occurred with the introduction of naphthenic acids. (see Fig. 48). It is clear that in contrast to experiments with the introduction of naphthenic acids during the introduction of increased quantity of cobalt naphthenate, the protective effectiveness of the film is improved. However, in connection with the short duration of the existence of such an effective film (due to the excess acidity of cobalt naphthenate) the introduction of cobalt naphthenate leads as a result to an increase in corrosion. In other words, as it seems to us, the anticorrosive effect from the introduction of salt essentially leads to nothing because of the reverse action of the surplus of naphthenic acids contained in the cobalt naphthenate.

On the basis of results of investigations mentioned above, it is possible to assume that with the introduction into the oil with an anticorrosive sulfur-containing additive of organic salt, which does not possess excess acidity, the effectiveness of action of the anticorrosive additive should be increased. Proceeding from this assumption we conducted experiments on oil MT-16 with the same additive with the introduction of a different quantity of neutral calcium sulfonate — 1, 3, 6 and 12%. Generalized results of these experiments at a temperature of the oil of 140°C are shown in Fig. 54, from which it is clear that in contrast to the cases examined (see Figs. 48 and 53) with an increase in content in oil of neutral calcium sulfonate the time of existence of the film on the lead surface is increased considerably. With this the quantity of film is increased insignificantly, and the corrosion decreases sharply. Thus the assumption was confirmed about the fact that with the introduction of calcium sulfonate into the oil with an anticorrosive sulfur-containing additive the effectiveness of action of the latter is increased.

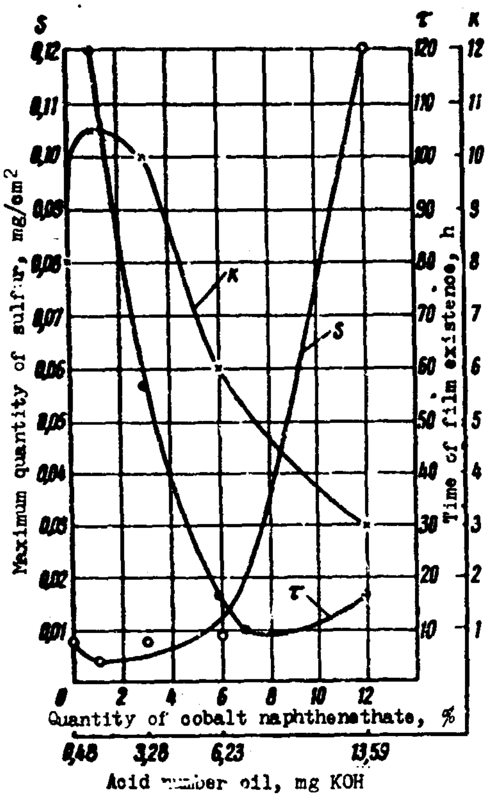

Fig. 53. Influence of naphthenate of cobalt on the protective effectiveness of films formed barium disulfide alkylphenolate on lead. Designations are the same as those in Fig. 48.

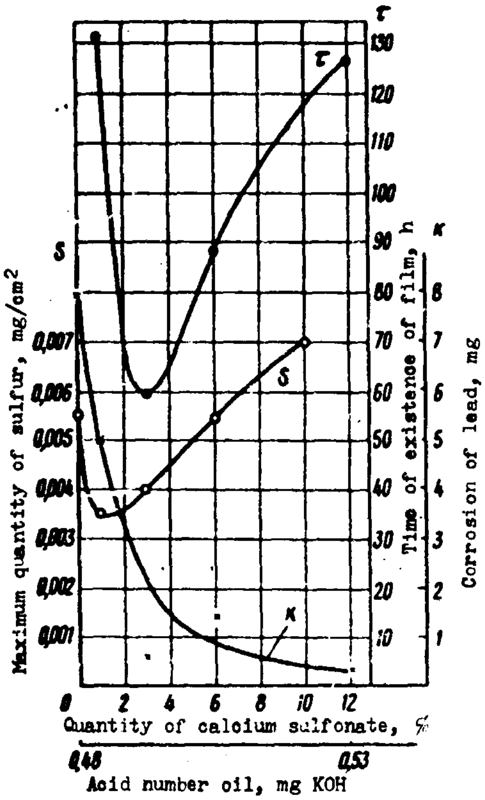

Fig. 54. Influence of neutral calcium sulfonate on protective effectiveness of films formed by barium disulfide alkylphenolate on lead. Designations are the same as those in Fig. 48.

A check was made whether or not the calcium sulfonate possesses the ability to retard corrosion of the surface of lead under the action of products of oxidation of the oil. Figure 55 shows results of these experiments with a different content of neutral calcium sulfonate - 1, 3 and 12% in oil MT-16 at 140°C in comparison with experiments on the same without additive and with 3% additive of barium disulfide alkylphenolate. As can be seen from Fig. 55, with the introduction into oil MT-16 of neutral calcium sulfonate the corrosion of lead effectively decreases. With this the higher the content of calcium sulfonate in oil, the more effective the corrosion is retarded. Thus the neutral calcium sulfonate not only increases the effectiveness of anticorrosive action by the sulfur-containing additive but also is an anticorrosive product itself. Calcium alkaline sulfonate of [PMSYa] (ПМСЯ) (Fig. 56) possesses similar action.

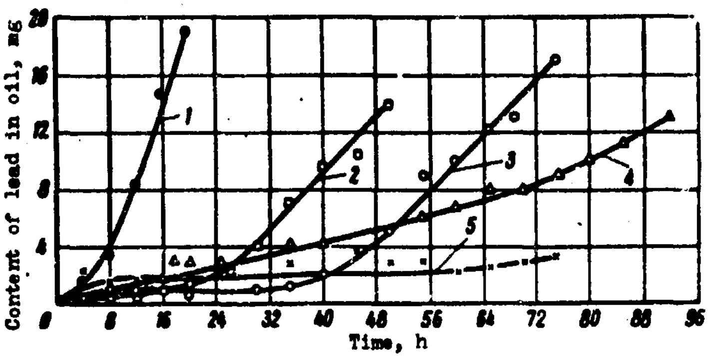

Fig. 55. Influence of neutral calcium sulfonate on the corrosion of lead under the action of oil MT-16. Temperature of oil, 140°C. 1 - MT-16; 2 - MT-16 + 1% calcium sulfonate; 3 - MT-16 + 3% calcium sulfonate; 4 - MT-16 + 3% barium disulfide alkylphenolate; 5 - MT-16 + 12% calcium sulfonate.

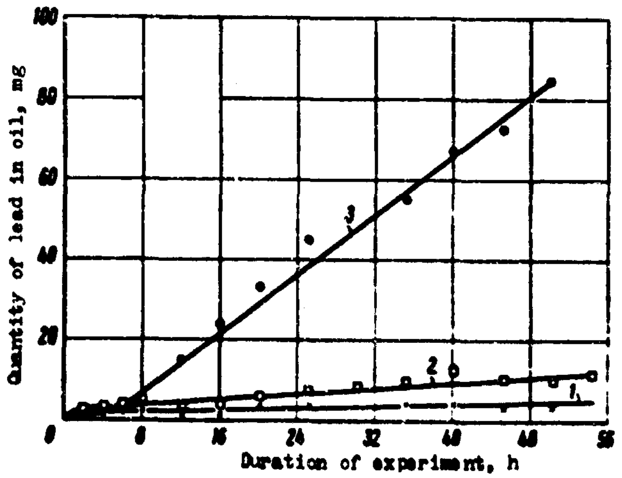

Fig. 56. Influence of alkaline calcium sulfonate on corrosion of lead under the action of oil MT-16. Temperature of oil, 140°C. 1 - MT-16 + 12% PMS; 2 - MT-16 + + 3% PMS; 3 - MT-16.

Investigation of Anticorrosive Action of Organophosphorus Additives

An investigation is conducted of the formation by phosphororganic compounds (tributyl phosphite and tryphenyl phosphite), labeled by P^{32}, of protective films on the surface of lead with simultaneous determination of the kinetics of corrosion of the latter. Figure 57 shows, for example, results of experiments on oil MT-16 with 0.5% tributyl phosphite at a temperature of oil of 140°C [121, 122, 124]. As can be seen from Fig. 57 the quantity of film forming on the surface of lead after achievement of the maximum value in the time interval of 12-16 hours starts to decrease; however in contrast to experiments with sulfur-containing additives the phosphorus does not depart completely from the surface of lead. Corrosion of lead is thus retarded as long as the quantity of film does not reach a maximum. After transition of the curve, reflecting the quantity of film through the maximum the corrosion rate sharply increases.

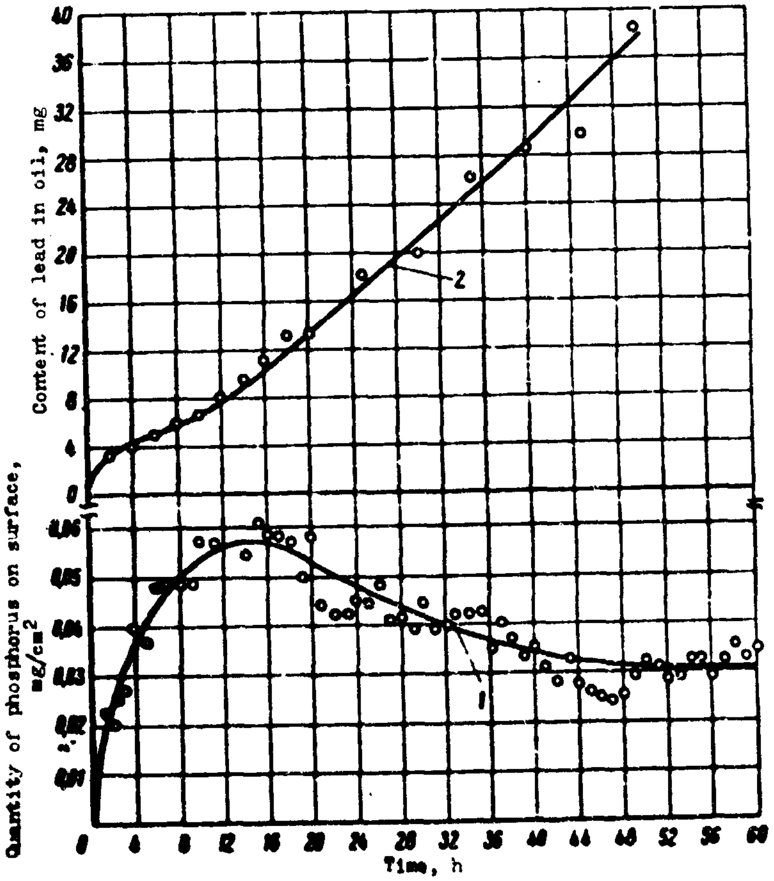

Fig. 57. Kinetics of the formation of protective film on lead (1) tributyl phosphite (0.5% in oil MT-16) and kinetics of corrosion of lead (2) at a temperature of oil of 140°C.

To investigate the character of processes of the formation and destruction of protective films, created by phosphoroganic compounds on the surface of lead, and the connection of them with the kinetics of corrosion we conducted experiments on oil MT-16 with 0.5% triphenyl phosphite, labeled in one case by the isotope P^{32} and in another case[1] by C^{14} at temperatures of the oil of 110°, 140°, 170° and 185°C. Figure 58 shows, for example, results of the experiment at 170°C. Analogous movement of curves reflecting kinetics of the formation by an additive of the protective film, recorded by radiation of isotopes C^{14} and P^{32} during the first 20 hours, and also the correspondence of quantities of phosphorus and carbon on the surface of lead for the same time to their relationship in the molecule of the additive indicate that in this time period the protective film will be formed by molecules of the additive with formation of a complex compound [124]. After 20 hours, as one can see from Fig. 58, the quantity of film recorded by radiation of C^{14}, starts to decrease, which indicates the starting destruction of additive in the oil, and with this the corrosion rate starts to increase. With full disappearance from the surface of lead of the film recorded by a carbon tracer, a secondary increase in the corrosion rate is observed. The phosphorus recorded by radiation of the isotope P^{32} continues to be preserved on the surface for more than 140 hours.

Thus processes of the formation and destruction of protective films on the surface of lead by phosphororganic and sulfur organic compounds have a similar character with the only difference that the sulfur, after destruction of molecules of the additive departs from the surface of the metal but the phosphorus is preserved on it since phosphides of metals are insoluble by acids.

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[1] Synthesis of the additive, labeled by radio isotope C^{14}, was conducted on the basis of phenol containing one atom of C^{14}.

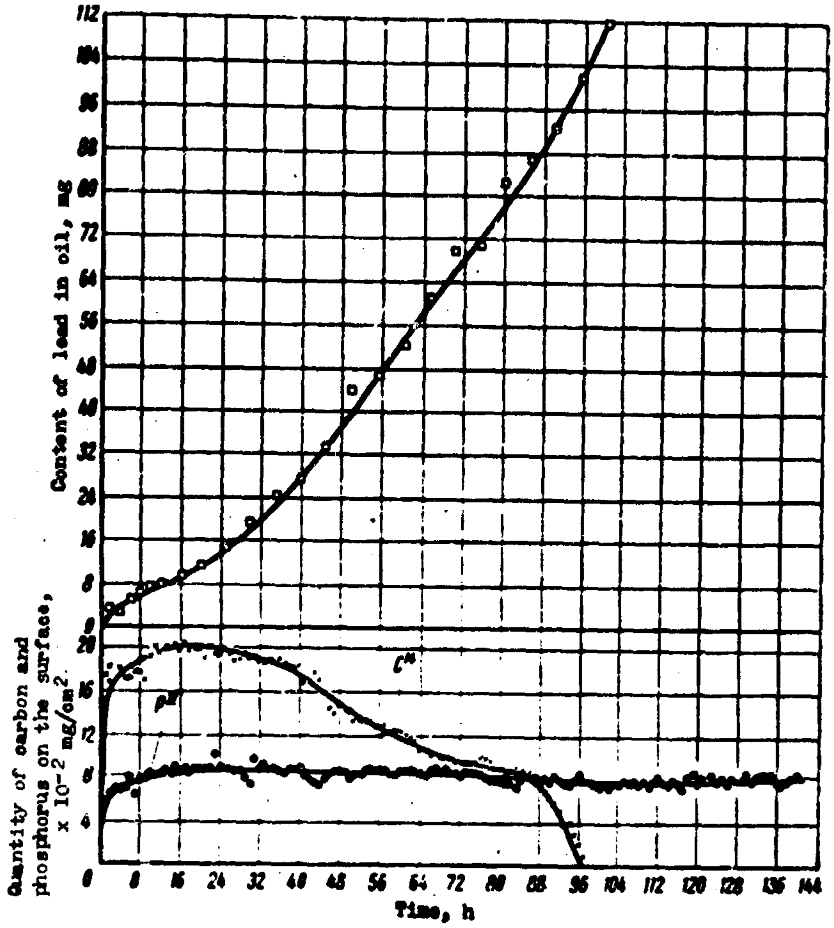

Fig. 58. Kinetics of the formation of protective films on lead by triphenyl phosphite, labeled P^{32} and C^{14}, and kinetics of the corrosion of lead. Oil MT-16 + 0.5% triphenyl phosphite. Temperature of oil, 170°C.

Mechanism of Destruction of Protective Films Formed by Anticorrosive Additives

Above there was shown the influence of organic acids and their salts (products, which are usually stored in motor oil with its oxidation during operation of the engine) on processes of formation and destruction of protective films on the surface of lead created by anticorrosive additives. With the usual concentrations of these products observed during oxidation of oil in the engine, there occurs intense destruction of protective films: the quantity of them on the surface of lead decreases, and the duration of the existence is reduced. However, the interaction of organic acids with the surface of lead in the presence of anticorrosive additives in oil is not studied.

To study the interaction of organic acid with the surface of lead there are conducted experiments [123] on oil MT-16 with various concentrations (0.014, 0.05; 0.1 and 0.5%) of tridecylic acid $CH_3(CH_2)_{11}C^{14}OOH$, labeled by isotope C^{14}. Experiments were conducted on the Pinkevich apparatus at a temperature of oil of 140°C (Fig. 59).

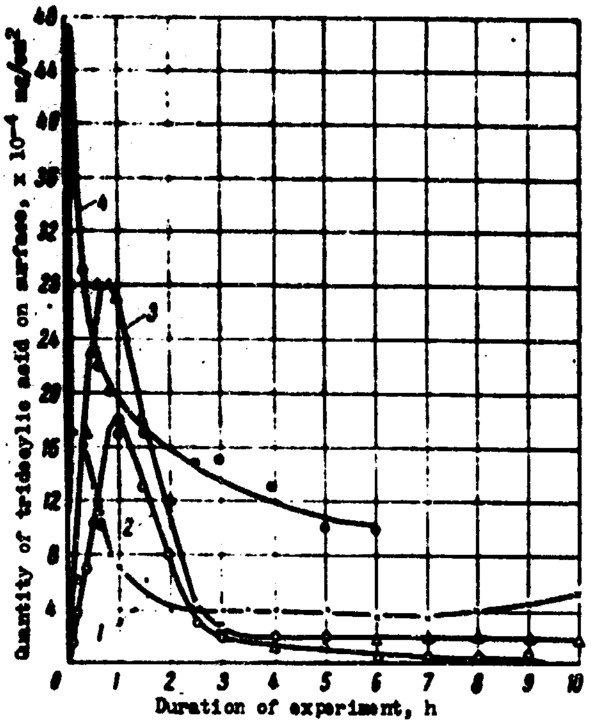

Fig. 59. Influence of the concentration of tridecylic acid on its interaction with a lead surface. Temperature of oil, 140°C: 1 - MT-16 + + 0.1% acid; 2 - MT-16 + 0.05% acid; 3 - MT-16 + 0.014% acid; 4 - MT-16 + 0.5% acid.

As can be seen from Fig. 59, the acid intensively interacts with the surface of lead, and then a "film" from products of the chemical reaction between the acid and lead will be formed. Such results correspond to data of other authors [126-128], who observed with the help of labeled organic acids the formation of films from products of reaction on surfaces of metals. As one should have been led to expect, these "films" do not retard the corrosion of lead, which is clear from Fig. 60.

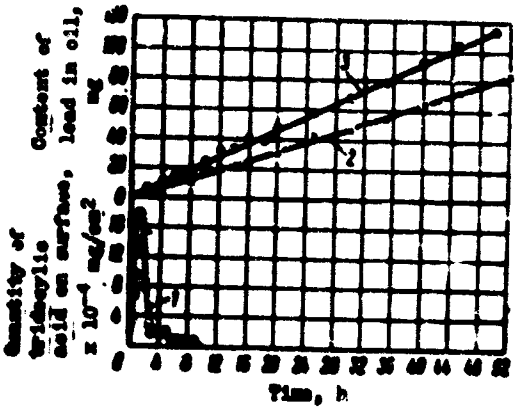

Fig. 60. Kinetics of the interaction of tridecylic acid (0.05% in oil MT-16) with the surface of lead (1) and kinetics of the corrosion of lead (3). Temperature of oil, 140°C. For a comparison on the upper graph the corrosion of lead under the action of oil MT-16 is shown (2).

Figure 60 gives results of experiments on oil MT-16 with 0.05% tridecylic acid, labeled by isotope C^{14}, in which there was investigated the formation of the "film" by acid on the surface of lead and corrosion of the latter.

The anticorrosive additive in oil into which acid is introduced should prevent intense interaction of acid with the lead, i.e., on the surface of the lead there should be revealed a smaller quantity of labeled acid. Experiments on oil MT-16 with 0.7% diphenol sulfide are conducted in which different quantities of labeled tridecylic acid (0,014; 0.05; 0.1; 0.5 and 1%) is introduced. The experiments were conducted at a temperature of oil of 140°C.

Figure 61 gives results of experiments with 0.05% acid in oils with an additive and results of experiments with the quantity of acid in oil without an additive. These experiments gave a somewhat unexpected result: although corrosion of lead in oils with an additive with the introduction of acid was less than that in oil without an additive, nonetheless the quantity of "film" formed by tridecylic acid on the surface of lead in the presence of an additive is almost one order of magnitude larger. How is it possible to explain such an effect?

Corrosion of nonferrous metals under the action of high-molecular acids occurs either through hydroxide of metal [129] or through oxide of metal [130]. We conducted experiments with the blowing through of air and technical nitrogen (0.6% oxygen) through naphthene paraffin fraction of oil MC-20 with 0.05% tridecylic acid, labeled by isotope C^{14}, into which lead plates were placed. Before the experiment there were mechanically taken oxide films from the surface of the plates immersed in oil. Figure 62 gives results of these experiments showing that with the blowing of air through the oil there occurs more intense interaction acid, labeled by the isotope C^{14}, with the surface, i.e., the acid interacts not with the metallic lead but with its oxide. Consequently, the "film" formed by the tridecylic acid on the surface of lead, should not, apparently cover the whole surface.

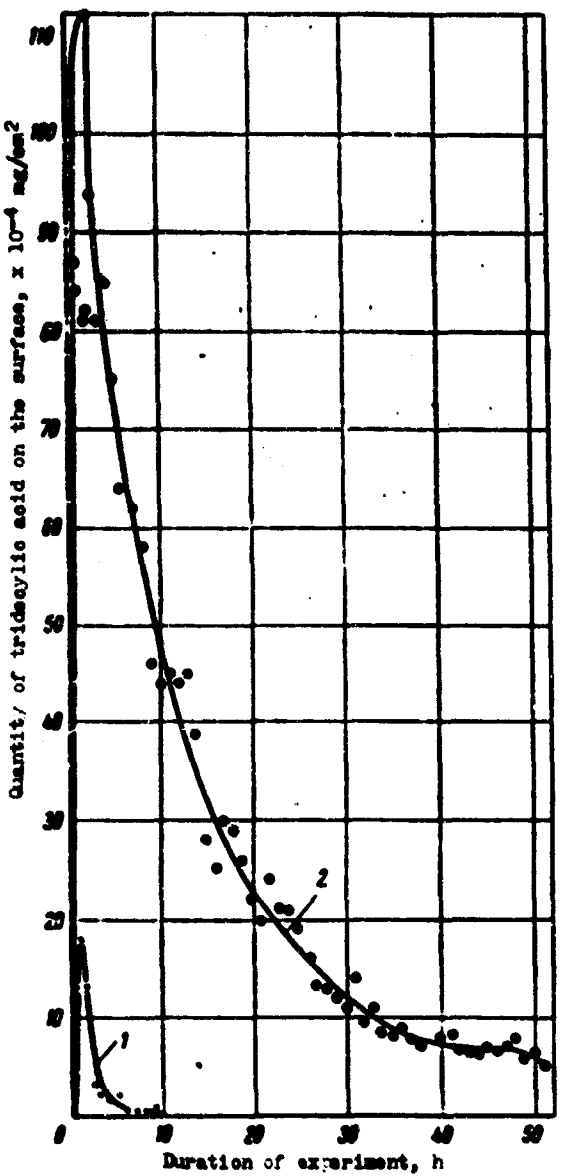

Fig. 61. Influence of anticorrosive additive on the interaction of tridecylic acid with a lead surface. Temperature of oil, 140°C: 1 – oil MT-16 + 0.05% tridecylic acid (C^{14}); 2 – MT-16 + 0.7% diphenyl sulfide + 0.05% tridecylic acid (C^{14}).

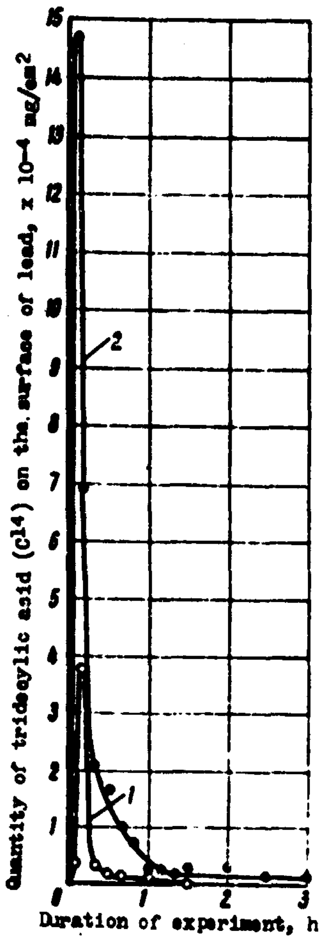

Fig. 62. Influence of air (2) and nitrogen (1) on the intensity of interaction of tridecylic acid (0.05% in naphthene paraffin fraction of oil MC-20) with the surface of lead at 140°C.

In the presence of the additive in oil the acid interacts, apparently, not only with oxide and (or) hydroxide of lead but also with sections of the surface on which the additive formed the complex with the metal. It is possible that this occurs as a result of solvation of these complexes by polar molecules of the acid. Results of a specially conducted additional experiment lead to the same assumption: the lead sample first worked in oil with an additive (0.7% diphenylsulfide and then in oil with labeled tridecylic acid. The quantity of acid revealed on the surface of the plate appeared approximately 2 times larger than during operation of the plate whose surface did not undergo interaction with the additive. Analogous results were found in experiments on oil MT-16 with 0.5% triphenylphosphite (temperature of oil, 185°C): as can be seen from Fig. 63, the quantity of "film" formed by tridecylic acid (labeled by isotope C^{14}) on the surface of lead is sharply increased, if in the oil a phosphoric additive is contained.

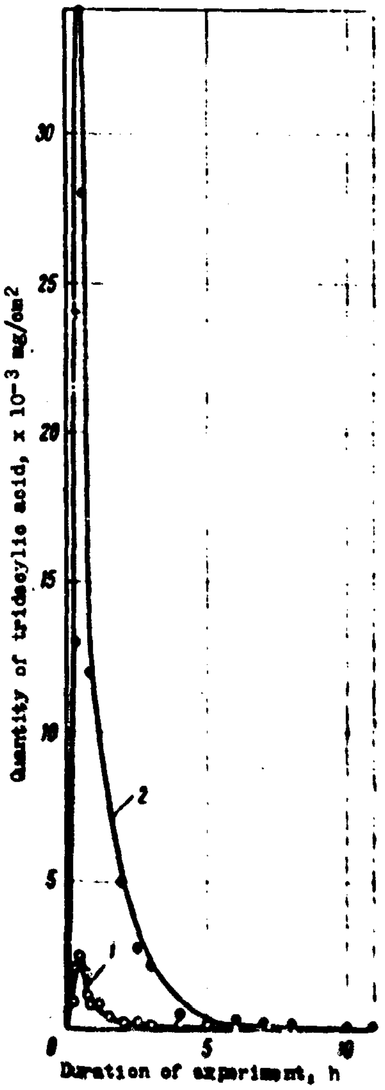

Fig. 63. Influence of anticorrosive additive on the intensity of interaction tridecylic acid with the surface of lead. Temperature of oil, 185°C: 1 – MT-16 + 0.05% tridecylic acid labeled C^{14}; 2 – MT-16 + 0.05% tridecylic acid, labeled C^{14}, + 0.5% triphenyl phosphite.

Processes of interaction of the additive and acid with surface of lead were studies more in detail in experiments on oil MT-16 with 2.8% diphenyl sulfide, labeled by isotopes S^{35} and C^{14}, and 0.066% stearic acid and experiments with the same unlabeled additive and 0.5% tridecylic acid, labeled by C^{14} [122, 123]. Figure 64 shows results of these experiments. Of special importance is the synchronism in the formation and destruction of films created by the additive and the "film" created by the acid. With the disappearance of films from the surface of lead synchronism is observed at first between the lowering of the quantity of the film, observed by radiation of the labeled radicals of the additive, and the "film" formed by the acid, and then between the lowering of the quantity of film observed by radiation of radio isotopes S^{35} and the "film" formed by the acid. It is possible to assume that the synchronism of departure from the surface of lead of the acid and radicals of additive is connected with the fact that the acid due to polarity solvates the radical of the additive which formed the complex with the metal and, because of greater strength of the bond of sulfur with the metal than with the radicals, detaches the latter and vanishes together with them from the surface. The synchronism of departure of the "film" which formed the acid and film, observed by radiation of the sulfur, is connected with the chemical interaction of the acid with the lead sulfide (formed after destruction of the complex of additive with metal) with the formation of salt of lead dissolved in oil with the separation of hydrogen sulfide. A more intense interaction of organic acids with sulfide of metals than with their oxides is noted in literature [131]. With this, apparently, is connected the complete departure of sulfur from the lead surface.

Thus, in general, according to the hypothesis expressed by us reactions which occur on the surface of lead with the formation and destruction of protective films, created by sulfur-containing anticorrosive additives, can be represented in the following way:

$$Pb + SR_2 \rightarrow PbSR_2;$$
$$PbSR_2 \rightarrow PbS + R_2;$$
$$PbS + 2RCOOH \rightarrow Pb(RCOO)_2 + H_2S.$$

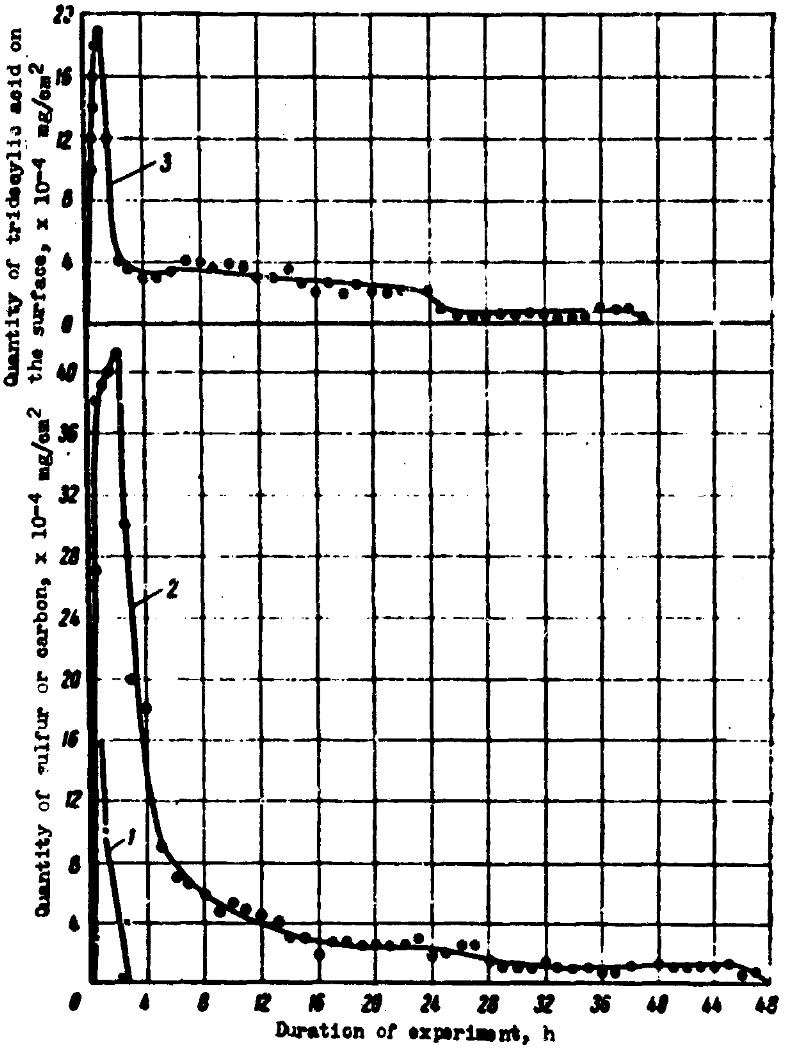

Fig. 64. Kinetics of interaction of diphenyl sulfide, labeled by isotopes S^{35} and C^{14} with the surface of lead in the presence of stearic acid at a temperature of the oil of 140°C: 1 – MT-16 + + 2.8% diphenyl sulfide (C^{14}) + 0.066% stearic acid; 2 – MT-16 + 2.8% diphenyl sulfide (S^{35}) + + 0.066% stearic acid; 3 – kinetics of interaction of the acid (C^{14}) with the surface of lead in the same conditions.

The synchronism of departure from the lead surface of acid and radicals of the additive was observed also in experiments with a phosphorous-containing additive. Figure 65 gives results of experiments on oil MT-16 with 0.5% triphenyl phosphite, labeled by isotope C^{14}, and 0.066% stearic acid and on the same oil with 0.05% tridecylic acid, labeled by C^{14}, and 0.5% unlabeled triphenyl phosphite. As can be seen from Fig. 65, synchronism is observed in the departure from the lead surface of radicals of the additive and "film" formed by the acid. In contrast to experiments with a sulfurous additive in experiments with a phosphorus-containing additive complete and simultaneous departure of the acid "film" and radicals of additive. Such a phenomenon, apparently, can be explained by the fact that the acid does not react with the lead phosphide forming with the destruction of the complex of the additive with metal as a result of solvation of radicals of the additive assumed by us. This is probably explained by our above examined very prolonged preservation of phosphorous on the lead surface after departure of radicals of the additive.

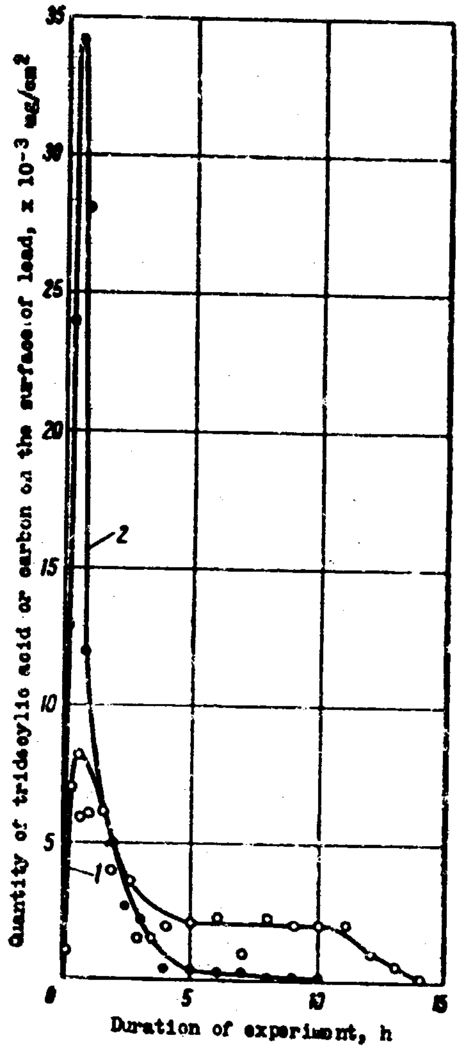

Fig. 65. Kinetics of the formation and destruction of films created triphenyl phosphite and tridecylic acid on the surface of lead. Temperature of oil, 185°C: 1 – MT-16 + 0.5% triphenyl phosphite (C^{14}) + 0.066% stearic acid; 2 – MT-16 + + 0.5% triphenyl phosphite + + 0.066% tridecylic acid (C^{14}).

Thus the application of labeled organic acid in combination with an additive labeled by sulfur or phosphorous and by a radical for the first time permitted studying the mechanism of destruction of protective films formed by anticorrosive additives to oils.

Investigation of the Protection by a Copper Component of Antifriction Alloys from Corrosion with the Help of Anticorrosive Additives

Since anticorrosive additives are obliged to provide effective protection of not only lead but also other nonferrous metals and alloys, in particular, copper and certain forms of bronzes, which are used for manufacture of different parts of contemporary engines, there was conducted an investigation of the mechanism of protection of copper from corrosion occurring under the action of products of oxidation of the oil. Experiments were conducted with oil MT-16 containing as additives individual sulfurous and phosphoric compounds: didecylsulphide, didecyldisulfide, decylmercaptan, dioctadecyl sulfide, dioctadecyl disulfide, diphenyl sulfide, triphenyl phosphite tributyl phosphite and tributyl tritiophosphite. The concentration of additives provided identical quantity of sulfur in oil. As can be seen from Table 19, a comparative protective effectiveness of these compounds with respect to the copper is analogous to that earlier observed with respect to the lead: the most effective protection is provided by the sulfide.

Table 19. Corrosion of copper and lead specimens in oil MT-16 with different additives for 30 hours of work of the Pinkevich apparatus at a temperature of oil of 140°C.

Tested oil	Corrosion, mg		Tested oil	Corrosion, mg	
	Copper	Lead		Copper	Lead
MT-16	0,060	48	The same + diphenyl sulphide	—	28
The same + didecyl disulfide	0,005	5	The same + diphenyl disulfide	0,070	32
The same + didecyl disulfide	0,180	32	The same + tributyl phosphite	0,016	21
The same + decyl mercaptan	0,120	25	The same + triphenyl phosphite	0,080	17
The same + didioctadecyl sulfide	0,015	13*	The same + tributyltrithiophosphite	0,010	23
The same + didioctadecyl disulfide	0,020	58*			

* At a temperature of oil of 170°C

Experiments on the study of corrosion of copper showed that the corrosion of copper in presence in oil of all the tested compounds and also under the influence of oil without an additive is 2-3 orders less than the corrosion of lead in presence of the same products (see Table 19).

For study of processes of the formation of protective films by anticorrosive additives on the surface of copper individual sulfurous compounds labeled by isotope S^{35} were synthesized: didecyl sulphide, didecyldisulfide, decylmercaptan. Experiments were conducted oil MT-16 with these compounds at temperatures of the oil of 110, 140, 170 and 185°C. Figure 66 gives temperature interaction curves of the examined sulfurous compounds with the surface of copper. Plotted along the axis of the ordinates are maximum quantities of sulfur film, which were observed by study of S^{35} at corresponding temperatures of the oil. Analogous experiments are conducted on samples of plumbous bronze, and the thus obtained temperature interaction curves of sulfurous compounds with plumbous bronze are shown in Fig. 67.

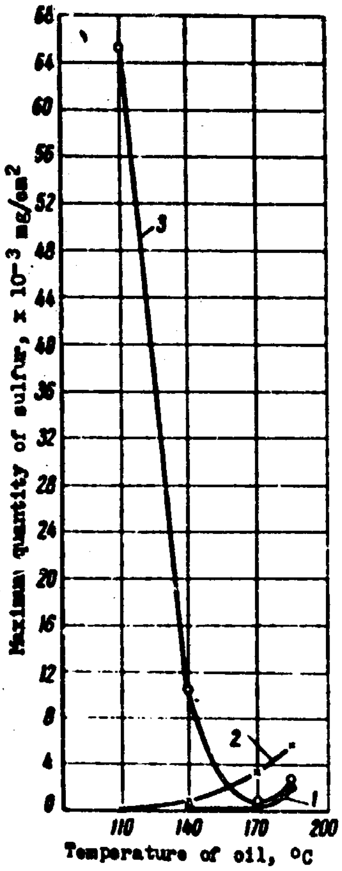

Fig. 66. Temperature interaction curves of different sulfurous compounds with the copper surface. Oil MT-16: 1 – didecyl sulfide; 2 – didecyl disulfide; 3 – decylmercaptan.

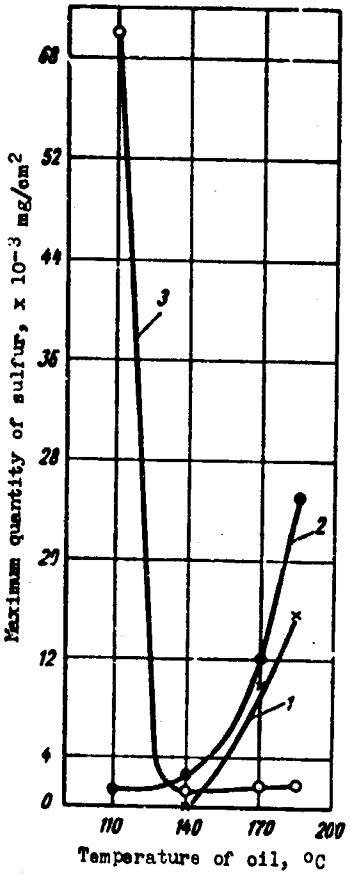

Fig. 67. Temperature interaction curves of different sulfurous compounds with the surface of plumbous bronze. Oil MT-16:
1 – didecylsulfide;
2 – didecyl disulfide;
3 – decylmercaptan.

From a comparison of Figs. 66 and 67 it is clear that there is an analogy in the interaction of sulfurous compounds with copper and plumbous bronze. One can also see a fundamental distinction in the character of the temperature interaction curves of dideculsulfide and didecyldisulfide on the one hand and decylmercaptan on the other hand: decylmercaptan intensely interacts with metal at low temperatures with the formation of a film of mercaptide, and sulfide and disulfide interact with metal at high temperatures with the decomposition of these compounds with splitting of the sulfur bound with metal. What has been said is confirmed by data obtained by us about the fact that the film of molecules of mercaptide at low temperatures retards the corrosion of copper, and the "films" formed by sulfide, disulfide and mercaptan at high temperatures are products of intense corrosion of copper (copper sulfide) and, naturally, do not protect the latter from corrosional destruction. Effective anticorrosive action of didecylsulfide at a temperature of the oil of 140°C is probably provided as a result of the formation of a complex of molecules of the additive and metal; this complex, however, is unstable and easily departs from the surface with washing.

Thus, by the conducted investigations it is established that in the range of temperatures of the oil, characteristic for operation of bushings of plumbous bronze in internal-combustion engines (110-140°C), the most effective protection of both lead and copper from corrosion is provided from the investigated sulfur-containing additives by organic sulfides. At temperatures higher than 140-170°C, characteristic for operation of units of friction of many contemporary high-loaded mechanism, the investigated sulfurous compounds, including sulfide, not only do not provide anticorrosive actions with respect to copper, but, conversely, sharply increase its corrosion.

Such corrosion of copper component of antifriction alloys, under the action of sulfur-containing components entering into composition of certain composition of additives to motor oils for contemporary engines can be eliminated by sulfonate component contained in the same compositions.

In connection with high anticorrosive effectiveness of calcium sulfonate established by us with respect to lead, this sulfonate was used as a second component in combination with the additive "sulphurized oil" [132], which had to cause intense corrosion of copper. Into oil MT-16 there was introduced 10% sulphurized oil and calcium sulfonate. In two experiments there was introduced 9% additive [PMS] (ПМС) and in two other experiments - 10% neutral calcium sulfonate. Results of these experiments showed that the intense corrosion of copper, caused by the action of sulfur, is very effectively retarded in presence of calcium sulfonates.

It was interesting to check to what is provided high anticorrosive effectiveness of calcium sulfonates with respect to lead and copper. There are conducted experiments on the Pinkevich apparatus at a temperature of the oil of 140°C with lead, copper, steel and glass disks. Into oil MT-16 was introduced 9% additive [PMSYa] (ПМСЯ), labeled Ca^{45}, and the presence of labeled calcium on the surface of the disks by the usual method was determined.

As can be seen from Fig. 68, on surfaces of lead, copper and steel there was observed a clearly marked formation of film by calcium sulfonate. On the surface of the glass the quantity of film is unstable.

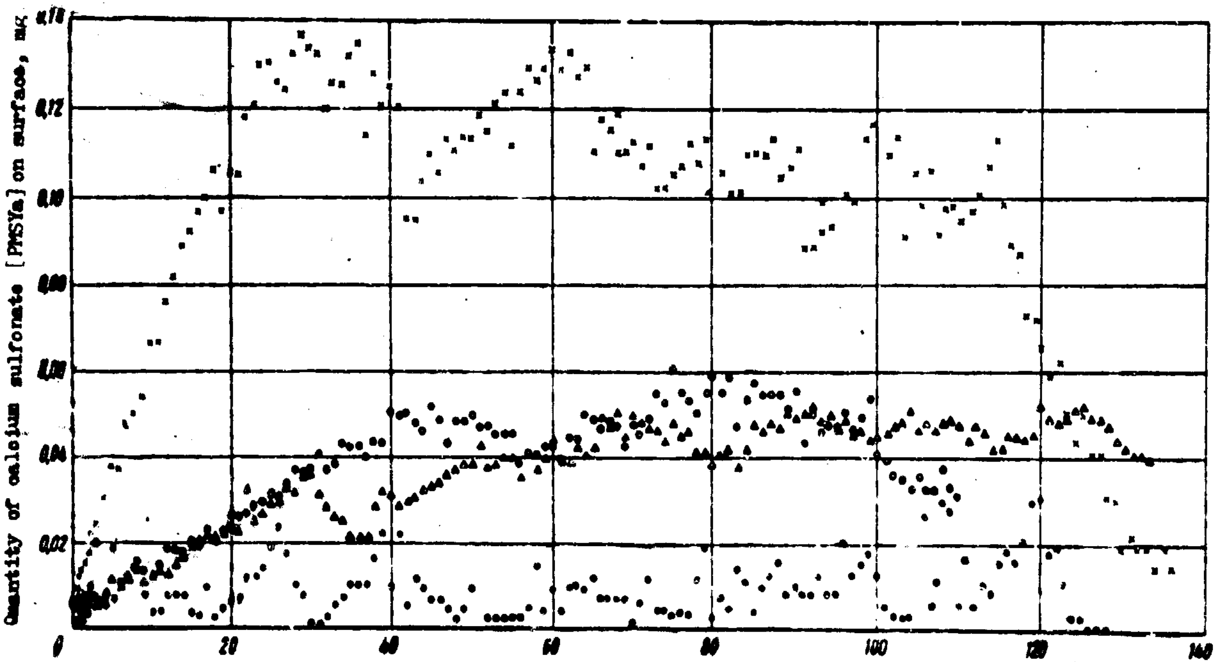

Fig. 68. Kinetics of the formation of film by labeled (Ca^{45}) calcium sulfonate (9% PMSYa in oil MT-16) on the surface of lead, copper, steel and glass. Temperature of oil, 140°C. X - lead; ○ - copper; Δ - steel; ● - glass.

Thus it is experimentally shown that the anticorrosive action of calcium sulfonate, just as the action of standard anticorrosive additives to oils, is based on the abrasion by the sulfonate of protective film on the metal surface.

Labeled calcium dinonyl sulfonate was used for investigation of the mechanism of action of calcium sulfonates as rust inhibitors [133]. This compound was obtained by direct interaction diphenyl naphthalene sulfonate acid with calcium chloride labeled Ca^{45}. In this and other works it is shown [133] that the investigation of the mechanism of action of inhibitors of corrosion with the help of the method of leveled atoms provide the most effective study of the localization of inhibitors on the surface of metal, the character of the bond of inhibitor with the surface of metal, the determination of optimum concentration of metal and so on.

CHAPTER 5

INVESTIGATION OF THE MECHANISM OF ACTION OF COUNTERSEIZING ADDITIVES

New Works in the Field of Study of the Mechanism of Action of Counterseizing Additives

The study of formation by additives of films on surfaces of nonferrous and ferrous metals still remains urgent in with the fact that these processes are the basis of the mechanism of action of not only anticorrosive but also counterwear and counterseizing additives to oils [113], 114, 126-128, 131, 134-251]. Thus with the help of the method of radioactive tracers Borsoff and Wagner [146] showed that the counterseizing additive dibenzyl disulfide will form a film on surfaces of gear teeth into the composition of which sulfur enters. These authors conducted investigations in bench test conditions on a gear reductor into which was filled mineral oil with dibenzyl disulfide labeled by isotope S^{35}, which was introduced into the oil from calculation of a 0.5% sulfur content. The tests were conducted at 3000 r/min under different loads. The duration of experiments was 30, 60 and 180 minutes. After a test under each load the gears were taken out and washed in a hydrocarbon solvent and dried, and with the help of an end-window Geiger counter the radioactivity on the surface of the teeth was measured. Distribution of the radioactivity on the surface of the teeth was studied by means of removal of radioautographs with the help of a special plastic holder, which was used for clamping the photographic film on the surface of the investigated tooth and insulation of the photographic film from the other adjacent sections of the gear (Fig. 69). Duration of the exposure was 16 hours. In these investigations it was established that the thickness of the counterseizing film, formed by dibenzyl disulfide on working surfaces of the gear teeth was increased with an increase in loads and depended on contact temperatures.

Fig. 69. Removal of a radioautograph from the surface of a gear tooth by means of plastic holder after a test on oil with counterseizing additive dibenzyl disulfide labeled by isotope S^{35}.

Later, with the help of analogous radioactive tracer methods of the investigation, Campbell [235] confirmed results obtained by Borsoff and Wagner [146].

The mechanism of action of counterseizing additives is examined in detail Beeck, Givens and Williamson [134] and is most clearly formulated by G. V. Vinogradov [136]: in standard conditions of friction on surfaces of steel parts there is an oxide film for which are characteristic considerable hardness, brittleness and refractoriness (more than for the metal itself). Such a film plays and important positive role with friction when low loads act. At high specific pressures the indicated combination of properties of the oxide film appears unfavorable. Deformation of metals more plastic than oxide films leads to a break of the films and to a direct contact of bared metals. Very high temperatures, which are developed during friction, can lead to considerable lowering of strength of the metal located under the oxide film or even to its fusion. As a result of the oxide film, which loses support, can be easily destroyed, and the metals in this case come in contact with each other. Under conditions of high loads such a contact of metals, in connection with peculiarities of their nature, leads to the gripping (welding) of surfaces of friction.

In the use of oils with organophosphorus additives in the zone of friction under the influence of high temperatures the compounds are decomposed, and on the surface of steel there will be formed iron phosphide. Films of iron phosphide are distinguished by considerable hardness and wear resistance. At the same time iron phosphide with iron can form a eutectic. Due to the considerable hardness of the phosphide film the wear with low loads proves to be low. With an increase in loads in microzones of specially high friction (projections on rubbing surfaces, etc.) the surface layer of the phosphide eutectic and metal is melted, which leads to a levelling off of the unevenesses – there appears a "polishing action" of the organophosphorus additives. At very high loads there occurs stripping of the phosphide layer and fusion of the eutectic, which envelopes the microzone on the rubbing surfaces. In these conditions the considerable hardness of the phosphide and the absence of its light wearability, which could ease the conditions of friction, are essential deficiencies of such a surface modification of metal.

In the use of oil with sulfur organic additives iron sulfide forming on the surface of steel, just as phosphide with iron, will form eutectic and is distinguished by well-known plasticity. Therefore, sulfide films on the surface of steel are characterized by relatively light wearability, which alleviates the condition of friction with a certain increase in the intensity of wear.

Iron chloride is distinguished by a much greater plasticity than that of iron sulfide. Due to the light wearability of films of iron chloride the conditions of friction with their presence on the surface of steel are considerably facilitated. An essential deficiency of chlorine derivitives as an additive to lubricating oils and also films of chlorides on rubbing surfaces is the easiness of hydrolysis of the majority of them and the formation of hydrochloric acid, which is extremely aggressive and a corrosionally effective product.

From what has been said above it follows that phosphide, sulfide and chlorine films on rubbing surfaces are distinguished by specific peculiarities. In certain conditions each of these forms of films, depending upon specific loads and other factors determining conditions of friction, provides minimum wear and damage to the rubbing surfaces.

Recently there appeared new works [227, 228] in which it is shown that the mechanism of action of phosphorus-containing counterseizing additives is distinguished from the mechanism formulated by Beeck and coauthors [134]. The most convincing are results of radioactive tracer investigations conducted by Barcroft and Daniel during the study of the mechanism of action of neutral organic phosphates as counterseizing additives [227]. The setting of these investigations was determined by results of an earlier conducted work of Barcroft [213] in which it was established that phosphorus-containing additives act different than sulfur- and chlorine-containing counterseizing additives. Such a conclusion is made on the basis of the fact that with identical counterseizing effectiveness the reactivity of organic phosphates is considerably lower than that of sulfur- and chlorine-containing additives.

Barcroft and Daniel [227] investigated the composition of films formed on surfaces of valve tappets of a four-cylinder carburetor automotive engine by triphenyl phosphate, labeled by isotope P^{32}. The engine operated in bench test conditions for 4.5 hours idling at temperatures of the cooling water of 85°C and oil in the crankcase of 93°C. The tests conducted with the use of valve tappets of cast iron and steel with different treatment of the surfaces. On half of the valves there were used the standard springs and on others, springs providing increased pressure.

The tests were conducted with a motor oil containing antioxidant, dispersive and polymeric additives and also 1% triphenyl phosphate as a counterseizing additive. The triphenyl phosphate contained 2.5% of the additive labeled by isotope P^{32}. The specific activity of the oil with additives was 3 μCi/g. With the help of infrared spectroscopy there was not revealed acid salts of phosphoric acid either in the triphenyl phosphate or in the labeled triphenyl phosphate.

After the tests the valve tappets taken from the engine were repeatedly washed in boiling benzene for removal of the oil, with the help of a Geiger counter radioactivity on their surface was measured, and radio autographs for an estimate of the distribution of radioactivity on the surface were also taken.

To determine the composition of films formed in the process of tests by triphenyl phosphate on surfaces of valve tappets there was conducted a radiochemical analysis founded on the assumption that products, entering into composition of the films should include the following: constant triphenyl phosphate; iron phosphide solvent in minerals acids with separation of phosphine; iron phosphide insoluble in mineral acids; iron phosphate.

Basically the radiochemical analysis was reduced to dissolution of the surface layer (with a thickness of approximately 0.02-0.05 mm) of the working part of the tappet in diluted hydrochloric acid in an atmosphere of hydrogen and to the measurement of radioactivity pertaining to phosphides, inorganic phosphates and organic phosphates. With radiochemical analysis there is not found phosphide on the metal surface, but there are revealed triphenyl phosphate, phenyl phosphates and inorganic phosphates.

Meaurements showed that on surfaces of valve tappets on which springs are set providing increased pressure there was observed considerably greater radioactivity (at a pressure of 50% greater the radioactivity was 4 times more). Such results indicated the sharp increase in temperatures in zones of contact with an increase in loads. On the basis of the measurements Barcroft and Daniel calculated the following: if one were to take the geometric surface of the tappet as the effective and the entire film formed by the counterseizing additive consisting of iron phosphate, then the thickness of the film with the standard springs was 70 Å and in case of springs providing increased pressure, 280 Å. These values were of the same order as those revealed by Borsoff during the above-mentioned carrying out of radioactive investigations on gear teeth [146].

On the basis of results of bench motor tests of oil with triphenyl phosphate labeled by P^{32} Barcroft and Daniel came to the conclusion that counterseizing protection of the surface of metal was provided by the formation of phosphates and organophosphates of metals and not by the formation of phosphide eutectic according to hypothesis Beeck and coauthors [134]. Barcroft and Daniel present the possible mechanism of counterseizing action of triphenyl phosphate in the following form: polar triphenyl phosphate is adsorbed on the surface of the metal. During flare-ups of temperatures in the zone of contact of metals the adsorbed triphenyl phosphate is decomposed (possibly, with catalytical action of the metal or oxides) with the formation of phenyl phosphates, which react with the surface of the metal. With this there will be formed salts possessing a high melting point. At raised temperatures these salts are decomposed, forming phosphates of metals with high counterseizing properties.

Barcroft and Daniel also investigated different aryl phosphates, in order to establish what physical-chemical properties of these substances determine their comparative counterseizing effectiveness. Triphenyl phosphate, tritolyl phosphate and tricresyl phosphate were tested in an engine and on laboratory apparatuses; it was shown that their ability to prevent burrs of valve tappets falls in the following order: triphenyl phosphate > tritolyl phosphate > tricresyl phosphate. The ability of adsorption of these esters was investigated with powders of chemically pure iron. Isotherms of adsorption of esters from solutions in toluene at 20°C were constructed. It was established that there is an insignificant difference in the adsorption of esters. The same results were obtained and at 60°C. The authors came to the conclusion that the countersiezing effectiveness of aryl phosphates is not connected with their adsorptive ability.

Adsorption of acid monophosphates, extracted from all three of the studied esters, was investigated. The adsorption proved to be irreversible, but ditolyl phosphate and dicresyl phosphate were formed by a monolayer, whereas diphenyl phosphate was completely extracted from a solution in toluene. A temperature rise caused a growth in sorption. The same experiments as those with iron powders were conducted on powders of cast iron and chromium. On powders from chromium a smaller difference was revealed in the sorption of diphenyl phosphate and ditolyl phosphate than on powder from iron. Nevertheless, in all cases the greatest sorption was observed on triphenyl phosphate; this, in the opinion of Barcroft and Daniel, determines its the greatest counterseizing effectiveness.

Proceeding from the concept about the fact that there is considerable importance in the formation rate of acid phosphates from triaryl phosphates, the authors studied the comparative thermal and hydrolytic stability of triphenyl phosphate, tritolyl phosphate and tricresyl phosphate.

Thermal stability was determined by heating esters under conditions of contact with air at different temperatures. Through defined intervals of time the magnitude of loss of weight and change of acidity were determined. Results of these investigations are given in Table 20. From the table it is clear that the comparative thermal stability of aryl phosphates is the reverse of their comparative counterseizing effectiveness.

Table 20. Comparative thermal stability of different aryl phosphates.

Additive	Decomposition, weight %, at temperatures, °C	
	207(12 h)	250(5 h)
Triphenyl phosphate	0.3	0.7
Tritolyl phosphate	1.2	4.7
Tricresyl phosphate	2.5	7.6

Hydrolytic stability was determined by washing of esters by sulfuric acid and solutions of caustic soda of different concentrations. It was established that the comparative ability to hydrolysis corresponded to the comparative counterseizing effectiveness of aryl phosphates. Products of hydrolysis – diaryl phosphates – were durably and irreversibly sorbed on surfaces of metals and, apparently, chemically interacted with them. Such results of investigations led Barcroft and Daniel to the thought that the mechanism of counterseizing action of aryl phosphates includes their hydrolysis. This point of view was confirmed during tests of oil with different phosphates introduced from the calculation of an identical content of phosphorus (0.08%) in the oil on a laboratory apparatus, which constituted a system of gas distribution of a four-cylinder automotive engine with electrical drive. The load on springs of the valve tappets was selected in such a manner that the seizing in oil without additive was created in 2-3 minutes. Counterseizing effectiveness of additives was estimated by the duration of delay of the burr. Results of the investigations conducted are shown in Table 21.

Table 21. Comparative hydrolytic stability and comparative counterseizing effectiveness of different phosphates.

Additive	Relative ability for hydrolysis	Time up to seizing, min	Additive	Relative ability for hydrolysis	Time up to seizing min
Benzyl diphenylphosphate	100	>30	Triphenyl phosphate	50	15
Allyl diphenylphosphate	100	>30	Tritolyl phosphate	30	8
Ethyldiphenylphosphate	80	28	2-Ethylhexyl diphenyl phosphate	5	2—3
Octyl diphenylphosphate	50	15	Oil without additive	—	2—3

From Table 21 one can see the good correspondence between the ability for hydrolysis and counterseizing effectiveness.

Thus Barcroft and Daniel as a result of conducted radioactive tracer investigations, showed that the mechanism of counterseizing action of neutral phosphate esters includes the following stages: 1) sorption of ester on the metal surface; 2) hydrolytic decomposition of ester with the formation of acid phosphates; 3) interaction of acid phosphates with the metal surface with the formation metal-organophosphates; 4) decomposition of metal-organophosphates with the formation of phosphates of metals. Despite the point of view of Beeck and coauthors [134], the absence of the formation of phosphide eutectic on steel with the application of a counterseizing additive tricresyl phosphate is also established in the work of Godfrey [228].

In studying the mechanism of action tricresyl phosphate as a counterseizing additive, Klaus and Biberer [229] developed radioisotopic method of investigation of the compatibility tricresyl phosphate with different surface-active additives (detergent, dispersive and others). The method is based on measurement of the sorption of tricresyl phosphate, labeled by isotope P^{32}, on surfaces of metals in the presence of the studied additives. The authors showed that in presence of certain detergent additives counterseizing effectiveness of tricresyl phosphate descends.

The compatibility of counterseizing additives with antioxidant was studied in work [233]. Investigations were conducted on a friction machine with two ball thrust bearings. Change in the coefficient of friction was measured with a change in speed, load and temperature of the oil.

The considerable influence of antioxidant additives on the effectiveness of the action of counterseizing additives with their simultaneous presence in oil is established. Thus an increase in concentration (up to 5 wt. %) of the counterseizing additive – chlorinated paraffin in mineral oil – caused practically no change in the coefficient of friction, whereas the introduction into the oil with different concentrations of chlorinated paraffin of an antioxidant additive (0.4 wt. %) 2.6-diquaternary butyl-4-methylphenol sharply changed the coefficient of friction: with small concentrations of the counterseizing additive the coefficient of friction increased, and with an increase in the concentration it sharply decreased. Fluorescent X-ray analysis and electron-microscopic photographs permitted determining that in the presence of an anti-oxidizer, as a rule, the quantity of chlorine on the rubbing surface was doubled. On electron-microscopic photographs the rubbing surfaces after tests on oil with both additives appear differently than after a test on oil with only one counterseizing additive.

Of interest also is the investigation conducted by Rounds of the influence of the chemical composition of base oils on the change in coefficient of friction connected with the interaction of counterseizing additives with rubbing surfaces in presence of antioxidant additives.

Table 22, for example, gives results of the investigation of

Table 22. Influence of the chemical composition of base mineral oils on the coefficient of friction with a test of counterseizing additives and their compositions with 0.4% antioxidant additive (2.6-diquaternary butyl-4-methylphenol).

Counterseizing additive	Concentration of counterseizing additive %	Static coefficient of friction				Dynamic coefficient of friction				Quantity of basic component of counterseizing additive on rubbing surfaces			
		Oil A		Oil E		Oil A		Oil E		Oil A		Oil E	
		without antioxidant additive	with antioxidant additive	without antioxidant additive	with antioxidant additive	without antioxidant additive	with antioxidant additive	without antioxidant additive	with antioxidant additive	without antioxidant additive	with antioxidant additive	without antioxidant additive	with antioxidant additive
										Chlorine			
Chlorinated paraffin	0,5	0,94	0,87	0,94	2,60	0,98	0,97	0,81	0,83	3,7	4,7	8,4	2.1
	5,0	1,02	0,89	1,37	0,47	0,95	0,87	0,75	0,63	1,8	5,7	6,3	11,3
										Sulfur			
Sulphurized terpenes	1,0	0,84	0,89	1,04	1,05—1,55	0,96	0,98	0,70	0,79	8,6	2,3	38,2	38,8
	5,0	0,82	0,89	1,15	1,27	0,86	0,84	0,69	0,68	17,1	22,2	70,3	47,5
										Phosphorous			
Didodecylphosphate	0,5	0,83	0,75	0,76	0,64	1,00	0,89	0,89	0,96	26,5	25,3	43,7	18,2
	5,0	0,68	0,49	0,35	0,41	0,93	0,85	0,73	0,92	37,1	13,6	11,8	12,8

two base mineral oils: oil A – a distillate of oils of naphthenic base and oil E – the same distillate subjected to deep purification by sulfurous anhydride with final cleaning by sulfuric acid and bentonitic clay.

In examining results of investigations given in Table 22, Rounds considers that if components of base oils are the essential component part of counterseizing films, then the nature of the products forming with oxidation of base oils of different chemical composition should significantly have an effect on the possible interaction of them with surfaces of metals. These products, competing with counterseizing additives, can hinder the additives in interacting with the rubbing surfaces. In connection with this the role of antioxidizers can consist in the control of nature and quantity of products of oxidation on surfaces of metals with the application of base oils of different chemical composition. With this the antioxidant action can possess natural inhibitors of oxidation, which are contained in oils in different quantity depending upon the raw material from which the oil is obtained and on the depth of its purification.

Manteufel and others [236] developed the radioactive tracer method of the investigation of interaction of labeled counterseizing additives with rubbing surfaces under condtions of tests on the modified four-ball Shell instrument [216].

There are synthesized aryl alkyldisulphide, dithiophosphoric acid and oil-soluble polymer labeled by isotope S^{35} with high molecular weight, in which the complex organic sulfide, obtained on the basis of elementary sulfur, served as a bond between the radicals. Dithiophosphoric acid, labeled by isotope P^{32}, is also synthesized. As the investigated counterseizing additive there was used composition of all three products – aryl alkyldisulfide, dithiophospsoric acid and a sulfur-containing high-molecular polymer. In each series of experiments only one of these products was labeled which permitted estimating exactly its role in the interaction with surfaces of metals with counterseizing action of composition.

The activity of the oil which contained the additive, labeled by isotopes S^{35} or P^{32}, was about 0.01 μCi/g of the oil. For one test in the four-ball instrument 20 g of oil are necessary.

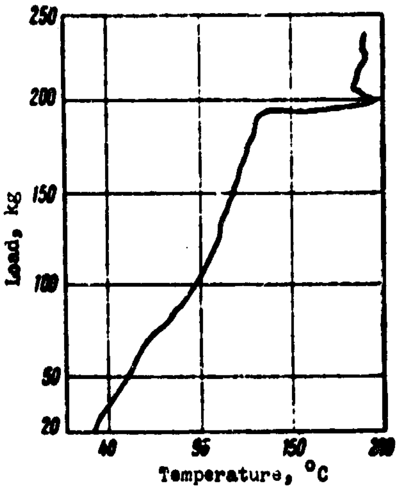

Fig. 70. Curve of the change in temperature of oil with a change in loads during a test of oil with counterseizing additive on the four-ball Shell instrument.

Every series of experiments started from a test of the oil with the labeled composition on the four-ball instrument with an increase in the loads every other minute by 10 kg, and altogether from 20 to 350 kg. The self-recording apparatus, which was equipped on the four-ball instrument, allowed a continuous recording of the change in temperature of oil in the zone of friction with a change in loads on the balls. Figure 70 shows such a curve recorded during a test of an oil with the examined composition. In the conditions shown of the increase in loads up to 350 kg the temperature of the oil was increased up to 200°C.

After the first test and the obtaining of a curve of the change in temperature of the oil with an increase in loads, there were conducted a series of experiments each of which was interrupted after achievement of the selected load, which was increased from experiment to experiment up to maximum load of 350 kg. Figure 71 shows curves of the change in temperature of the oil with a change in loads recorded with the carrying out of such a series of experiments. Upon completion of each of these experiments the diameter of the spot of wear on the surface of the balls and the quantity of labeled sulfur or phosphorus tracer at the spot of wear with the help of a Geiger counter and radiometric instrumentation were measured.

The conducted standardization permitted determining the quantity of sulfur or phosphorus in micrograms. Radiometric measurements provided sensitivity of determinations of the orders of 0.001 μg with an accuracy of 10-15%. In the conducted investigations of the quantity of sulfur or phosphorus at wear spots on the surface of the balls varied from 0.01 to 50 μg.

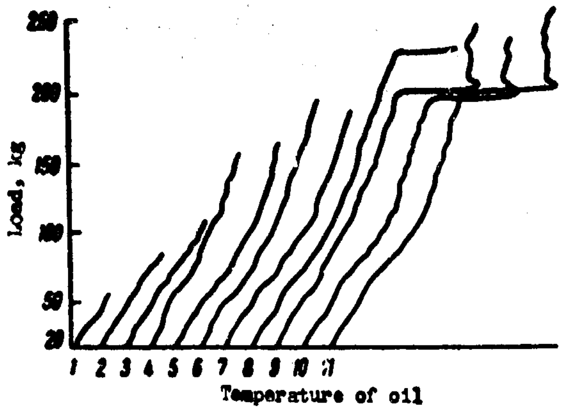

Fig. 71. Curves of the change in temperature of oil with a change in loads obtained during a test of oil with a composition of counterseizing additives on a four-ball instrument in a series of experiments each of which was conducted up to the achievement of the assigned load. The curves are shifted along the axis of the temperature so that it was possible to put them on one common diagram.

According to data of radioactive investigations conducted on four-ball instrument, there were constructed graphs in these coordinates: quantity of sulfur or phosphorus at the wear spot on the surface of the ball (in micrograms per square millimeter), referred to the concentration of labeled component in oil (in milligrams per gram) - load on balls during the test (in kilograms). Figure 72 shows such graphs obtained with the investigation of the examined composition of additives in comparison with the curve of the change in temperature of oil during a change in load on the balls.

From a comparison of curves on Fig. 72 it is clear that the quantity of sulfur and phosphorus in spots of wear on the surface of the balls is increased with an increase in temperatures and especially sharply with a stepwise increase in temperatures of the oil, which is characteristic for the appearance and development of seizings and jammings. One can see also that in the investigated composition phosphorus was more chemically active in the interaction with surfaces of steel balls than sulfur entering into any of the three components - aryl alkyldisulfide, dithiophosphoric acid and sulfur-containing polymer.

As results of investigations showed, the content of phosphorus at spots of wear on the surface of the balls was 5-50 times more than the content of sulfur (depending upon the character of the compared sulfur-containing compound and temperatures during the comparison).

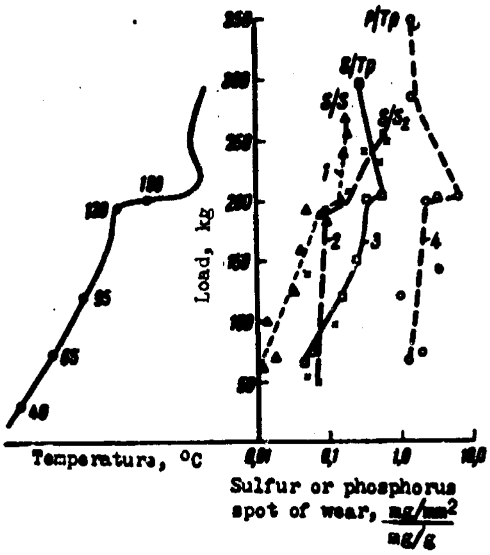

Fig. 72. Quantity of sulfur or phosphorus in spots of wear on the surface of steel balls according to data of tests of oil with a composition of labeled additives on the four-ball instrument under different loads: 1 – organic sulfide, S^{35}; 2 – aryl alkyl disulfide S^{35}; 3 – dithiophosphoric acid, labeled by S^{35}; 4 – dithiophosphoric acid, labeled P^{32}.

Manteufel and others revealed that phosphating of the surface of the steel balls increased the quantity of phosphorus at spots of wear but practically did not change the quantity of sulfur in them.

The difference in comparative reactivity of sulfur, which entered into composition of the three indicated components, proved to be considerably smaller than the difference between the reactivity of phosphorus and sulfur. As can be seen from Fig. 72, the greatest comparative reactivity was possessed by sulfur entering into the composition of the dithiophosphoric acid somewhat smaller was that of sulfur of aryl alkyldisulfide, and the least - sulfur of sulfide.

Sakurai and coauthors [149, 150, 237, 245] and Llopis and others [252] used labeled additives for the study of the mechanism of formation by counterseizing additives of films on rubbing surfaces of metals. Francis and Ellisson [210] conducted investigations in that same direction.

In recent years many authors have conducted radioactive tracer investigations of the mechanism of counterseizing action of dialkyl dithiophosphate additives [114, 131, 141, 144, 145, 209]. In these investigations, just as in work [236], there is basically studied the accumulation of components of dialkyl dithiophosphate additives – phosphorus, sulfur, zinc – on surfaces of metals under conditions characteristic for the application of counterseizing additives. Thus, Loeser and coauthors [145] showed that with the application of zinc dialkyl dithiophosphate the quantity of phosphorus on the working surface of valve tappets of the distributive system of the automotive engine, at temperatures higher than 120°C, increases considerably more intensely than the quantity of zinc (Fig. 73).

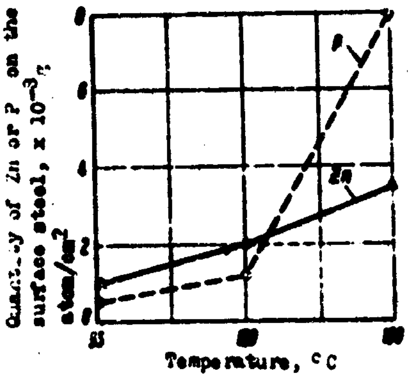

Fig. 73. Influence of temperature on the quantity of phosphorus and zinc forming a counteradditive film on a steel surface.

It should be noted that the study of the formation of films by based components of counterseizing additives on rubbing surface does not permit in full measure obtaining data on the counterwear effectiveness of these films.

Furey and Kunc [141] used irradiated Fe^{59} neutrons on valve tappets of an automotive engine for studying wear during bench tests and labeled by isotope Zn^{65} zinc dialkyl dithiophosphate for investigation of the formation of film on the surface steel under conditions of laboratory experiments. The authors did not establish the correlation between wear of the tappet and quantity of film on the steel surface.

Dorinson and Broman [222] and Sakurai with his colleagues [149], 150, 237, 245] made the first attempts of deeper study of the connection between chemical activity, i.e., reactivity of different sulfur-organic compounds with respect to steels, and their counterseizing effectiveness. Sakurai and his colleagues also started a comparative investigation of the speed of formation of sulfide films on rubbing surfaces of steels by different sulfur-organic additives and the speed of abrasion of these films.

G. V. Vinogradov [136] noted that substances utilized as counterwear additives should not intensively interact with metal at those temperatures which are characteristic for oil in volume, the corrosion of metals can occur differently, and the expenditure of additives is not by assignment. Therefore, the action of the additive should appear only at those sufficiently high temperature jumps which appear under conditions of very high loads and speeds, which cause burrs, jamming etc. Inasmuch as counterwear additives should be sufficiently active with respect to the metals, they can manifest to them a well-known corrosional aggressiveness. The whole difficulty of the selection of such additives is connected with the fact that the counterwear effect should be the greatest and the corrosional, the least. G. V. Vinogradov stresses that the solution to this problem is usually a compromise.

At the same time certain authors experimentally show and especially note that the greatest counterseizing effectiveness is the most chemically active, i.e., the most corrosion aggressive additives [150, 175, 193, 194, 222, 238]. In these investigations Braithwaite and Rowe [238] used counterseizing additives, labeled by isotope Cl^{36}.

Consequently, the indicated compromise path of selection can not provide creation of the most effective counterseizing additives to oils. This becomes especially evident if one were to consider the corrosional interaction revealed recently by Ellis and coauthors [225] and Moore and Lewis [226], on anti-friction bearings of counterseizing additives to transmission oils selected on the basis of the compromise approach and also ineffectiveness of counterseizing additives to oils established by G. V. Vinogradov and coauthors [253] in friction units of high-speed mechanisms. In these mechanisms, apparently, there is not created a sufficient reserve of time for the development of processes of decomposition of the additive and interaction of products of decomposition with surfaces of metals. The need to study and estimate the speed of interaction of counterseizing additives with surfaces of friction is noted in the work of Sellei [239]. In such conditions, and also in the case of specially high loads, as was shown in the work of Dolrinson and Broman [222], the counterseizing effect can provide only large concentrations of additives.

Investigation of the Mechanism of Anticorrosive Protection with the Application of Counterseizing Additives

During the study of the mechanism of action of anticorrosive additives to oils is shown above that the most effective protection of bushings of nonferrous metals and alloys from corrosion under the action of products of oxidation of oil is attained in cases when the protective film, created on the surface of metal, consists of molecules of an additive forming the complex with the metal. This led to the conclusion that the greatest anticorrosive effectiveness should be provided by polar sulfur- or phosphorus-containing compounds in whose molecules the indicated elements have the most durable bonds.

Results of the study of the mechanism of chemical destruction of protective anticorrosive films confirmed this conclusion: it is shown that destruction of the film, leading to a loss in anticorrosive effect, occurs by means of solvation and detachment of radicals of the additive by acids, and, consequently, the strength of the bonds of sulfur or phosphorus in molecules of the additive determines the duration of preservation of the anticorrosive effect other things being equal.

The investigations conducted permitted giving a clear determination of the fundamental distinction in requirements of chemical compounds in the selection of anticorrosive and counterseizing additives to oils. This distinction is reduced to the fact that anticorrosive additives, as was shown above, should possess durable bonds of sulfur or phosphorus in molecules, whereas counterseizing additives should easily detach the sulfur, phosphorus . chlorine for formation on the metal of corresponding sulfide, phosphides or chlorides at high contact temperatures. Such a fundamental distinction between the indicated forms of additives explains the greatest counterseizing effectiveness of chemically active compounds established by many authors, which are corrosionally aggressive with respect to the metals protected by them from seizing [136, 150, 175, 191, 193, 194, 222, 258, 259].

Very recently Allum and Ford [260] investigated a large group of different sulfur-organic compounds, studying the influence of the structure of such compounds on their counterseizing effectiveness. These authors showed that the less the strength of the bond between atoms of sulfur and carbon in the molecule, i.e., the easier the sulfur is detached, the higher the counterseizing effectiveness of the sulfur-organic compound. Thus, for mono- and disulfides the countersiezing effectiveness, according to data of tests on a four-ball apparatus, increased in the following order:

phenyl 1 < n-butyl < secondary butyl < tertiary butyl < benzyl.

Due to what has been stated above we came to the conclusion that the creation of the most effective counterseizing additives possible not only as a result of the usually used selection of chemical compounds, which would provide a sufficient counterseizing effect with minimum corrosional influence [136], but also by means of selection of two-component additives constituting the combination of the most effective counterseizing and anticorrosive components. With such composition of additives it is possible, apparently, to remove the effect of delay in the operation of counterseizing additives during work in friction units of high-speed mechanisms.

To investigate and select such two-component additives in laboratory conditions we developed radioactive tracer method of determination of the activity of counterseizing additives to oils [132, 254-256, 261, 262], inasmuch as the chemical activity of counterseizing additives determining their reactivity with respect to metals protected from burrs and jammings thereby determines their counterseizing effectiveness [150, 210, 222, 239, 255, 257].

The chemical activity of counterseizing additives was estimated in the determination of kinetics of dissolution in the oil of radioactive steel (irradiated by Fe^{59} neutrons) or copper (activated by the introduction of trace amounts of isotope Ag^{10} in the melted copper) under the action of the tested additives [132]. The selection of copper plates was determined by an interaction more active as compared to steel of copper with additives to oils with a fundamentally analogous character of the interaction of these metals with the studies compounds [258, 259]), which provided great sensitivity and shortness of investigations [259].

Table 23 gives results of the radiometric determination of chemical activity of counterseizing additives with respect to steel and copper. From the table it is clear that with the identical character of the comparative data the chemical activity of additives is determined with help of radioactive steel at temperatures of the oil of 200°C during 50-75 hours with small quantities of corroded metals, whereas with the help of radioactive copper the chemical activity can be estimated at a temperature of oil of 150°C less than for 5 hours with considerably greater quantities of metal, which passed over into the oil. Such results are fully connected with indications available in literature [258, 259]. Data of radiometric determination of the activity of counterseizing additives corresponded well to results of tests of these additives on four-ball apparatuses.

Table 23. Results of radiometric determination of the chemical activity of counterseizing additives.

Tested oil with additive	Quantity of iron in oil (mg) at 200°C for time t, h				Quantity of copper in oil (mg) at 150°C for time t, h			
	5	15	25	75	5	10	15	50
Oil of Orsk works [O.Z.] of selective purification from nonsulfurous oils (with viscosity v_{100} = 14 cSt + + 3% dibenzyl disulfide + + 7% chlorinated paraffin	0,008	0 014	0,018	0,180	4,81	15,6	18,2	–

There is investigated [255] the chemical activity with respect to radioactive copper of different sulfur- and chlorineorganic compounds and their combinations, finding application as counterseizing additives and introduced into different oils: DS-14 and oil of Orsk works [O. Z.] of selective purification from non-sulfurous oils (with a viscosity ν_{100} = 14 cSt). Figure 74, for example, gives results of the radiometric determination with the help of copper plates at a temperature of the oil of 150°C of the chemical activity of counterseizing additives introduced into oil DS-14. From Fig. 74 it is clear that the chemical activity of each of the components – chlorinated paraffin CP and dibenzyl disulfide [DBDS] (ДБДС) (or the additive [LZ-6/9] (ЛЗ-6/9) – ethylene dibutyl xanthate) is considerably less than the chemical activity of their mixture [255].

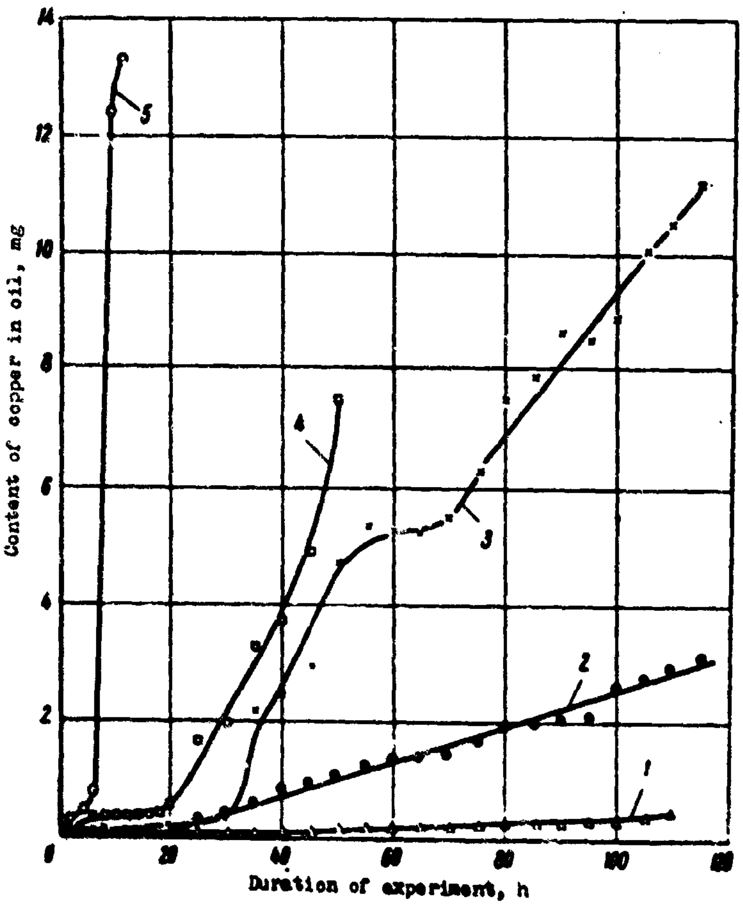

Fig. 74. Results of radiometric determination of chemical activity of counterseizing additives on the Pinkevich apparatus with the help of radioactive copper disks. Temperature of oil, 150°C. 1 – oil without additive DS-14; 2 – DS-14 + 5% CP (chlorinated paraffin); 3 – DS-14 + 5% LZ-6/9 (counterseizing additive ethylene dibutyl xanthate); 4 – DS-14 + 3% LZ-6/9 + + 7% CP; 5 – DS-14 + 7% CP + 3% DBDS (dibenzyl disulfide).

From the investigated counterseizing additives and their mixtures the greatest chemical activity was possessed by mixtures of 3% dibenzyl disulfide with 7% chlorinated paraffin and 3% LZ-6/9 with 7% chlorinated paraffin, for which these mixtures were used in further experiments for the selection of a second anticorrosive component with the creation of optimum compositions of counterseizing additives. According to data of tests on the four-ball apparatus this mixture provided the highest counterseizing effect, which is clear from Fig. 75. From a comparison of Fig. 74 and 75 it is clear that comparative data of the determination of chemical activity correspond to results of tests on four-ball apparatuses.

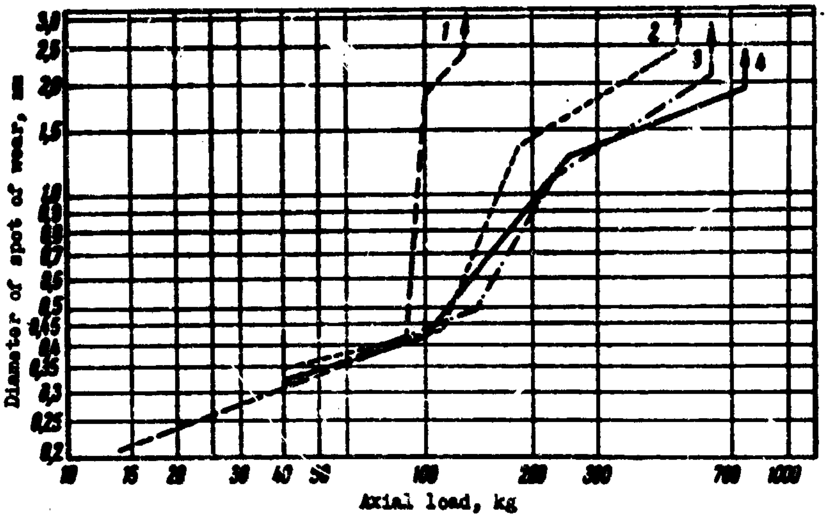

Fig. 75. Results of the determination of counterseizing effectiveness of additives on a four-ball apparatus: 1 – oil without additive DS-14; 2 – DS-14 + 5% LZ-6/9; 3 – DS-14 + 3% LZ-6/9 + 7% CP, 4 – DS-14 + + 3% DBDS + 7% CP.

Figure 76 gives results of radiometric determinations (with the help of copper plates at a temperature of the oil of 150°C) of the ability of certain additives to provide an anticorrosive effect in the presence of chemically active counterseizing additives.[1] As can be seen on Fig. 76, with the introduction of additives 1L and [PMS] (ПМС) an anticorrosive effect with respect to copper was observed. From Table 24 it is clear that additive 1L provided a similar effect with respect to steel, and according to data of tests on the four-ball apparatus the effectiveness of action of counterseizing additives was preserved [225].

From Fig. 77 it is clear that with the introduction of additives VNII NP-371[2] and phenyl-α-naphthylamine and anticorrosive effect in the composition with counterseizing additives was observed.

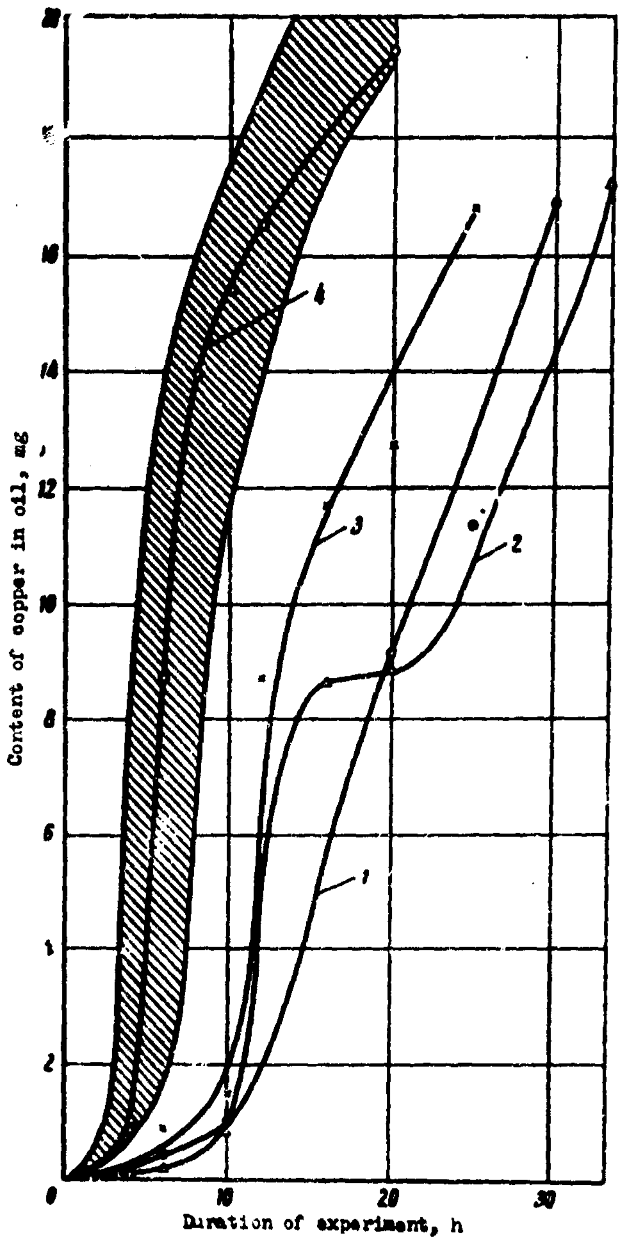

Fig. 76. Results of the radiometric determination of the effectiveness of different anticorrosive additives in composition with chemically active counterseizing additives. Copper radioactive disks. Temperature of oil, 150°C. 1 – oil O.Z.+ 3% DBDS + + 7% CP + 6% 1L (barium alkyl phenolate in a solution of hydroxypropyl alkyl phenol); 2 – oil O.Z. + 3% DBDS + 7% CP + 12% 1L; 3 – O. Z. oil + + 3% DBDS + 7% CP + 12% PMS (multiash-superalkaline-calcium sulfonate); 4 – O. Z. oil + 3% DBDS + 7% CP.

Table 24. Results of determination of corrosional aggressiveness and counterseizing effectiveness of of oil with additives.

Tested sample	Corrosion, mg		Results of tests on four-ball apparatus, maximum load up to jamming, kg
	Copper for 10 h at 150°C	Steel for 75 h at 200°C	
Oil of Orskiy works of selective purification from nonsulfurous oils (with viscosity ν_{100} = = 14 cSt)	0,03	–	79
The same oil + 3% dibenzyl disulfide + 7% chlorinated paraffin	15,6	0.18	126
The same oil + 3% dibenzyl disulfide + 7% chlorinated paraffin + 12% additive "1L".	0,8	0.04	126

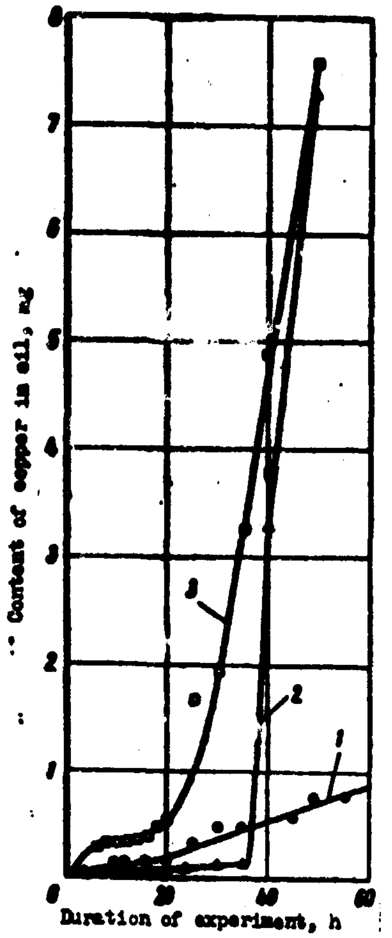

Fig. 77. Results of radiometric determination of anticorrosive effectiveness of certain additives in composition with chemically active counterseizing additives. Copper radioactive disks. Temperature of oil, 150°C. 1 – DS-14 + + 3% LZ-6/9 + 7% CP + 1% V-371; 2 – DS-14 + 3% LZ-6/9 + 7% CP + 0.3% phenyl-α-naphthylamine; 3 – DS-14 + + 3% LZ-6/9 + 7% CP.

Along with an empirical selection of anticorrosive components we conducted also radiometric investigation of anticorrosive properties of phosphorus-containing compounds [254-256] proceeding from the assumption about the fact that an effective protection of surfaces of metals from corrosive influence of atoms of chlorine and sulfur can be attained by means of the creation of not molecular but a denser atomic film, through which it is more difficult to penetrate to the surface to mobile atoms of chlorine and sulfur. It was assumed that such an atomic film can be created with the use of phosphorus-containing compounds proceeding from the data indicated above about the fact that phosphides of metals, in contrast to sulfides, are insoluble by acids, including products of oxidation of oils, and therefore for a long time and durably they hold onto surfaces of metals to which recently other researchers have turned attention [257]. The phosphorus-containing compounds should be soluble in the appropriate oil and should detach the phosphorus at temperatures considerably smaller then temperatures of decomposition of counterseizing components. Together with that it was assumed that the formation on the surface of metal of phosphide possessing counterseizing action [136] should not worsen the effectiveness of counterseizing components.

As can be seen from Figs. 78 and 79, with the introduction of phosphorus-containing additives (0.5% phenyl phosphite, 3% additive [DF-9] (ДФ-9), 3% additive DF-11) there was an effective decrease in corrosion of steel (at a temperature of oil of 200°C) under the action of a mixture of dibenzyl disulfide or LZ-6/9 with chlorinated paraffin. According to data on tests on the four-ball apparatus the counterseizing effectiveness did not worsen.

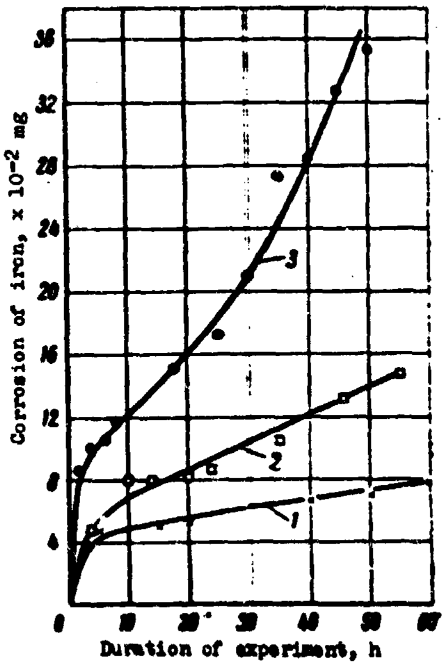

Fig. 78. Results of radiometric determination of anticorrosive effectiveness of phosphorus-containing in composition with chemically active counterseizing additives. Steel radioactive disks. Temperature of oil, 200°C. 1 – O. Z. oil + 3% DBDS + 7% CP + 0.5% TFF (triphenyl phosphate) 2 – O. Z. oil + 3% DBDS + 7% CP + 3% DF-9; 3 – O. Z. oil + 3% DBDS + 7% CP.

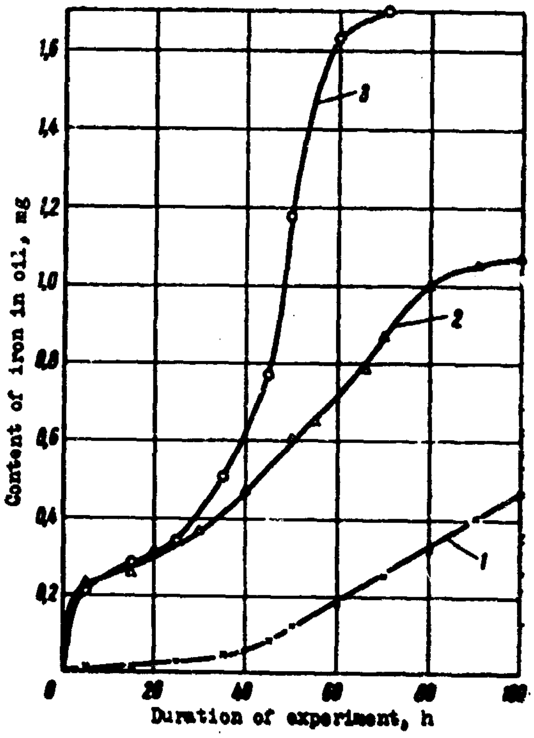

Fig. 79. Results of radiometric determination of anticorrosive effectiveness of phosphorus-containing compounds in composition with chemically active counterseizing additives. Steel radioactive disks. Temperature of oil, 200°C. 1 – DS-14 + 3% LZ-6/9 + + 7% CP + 0.5% TFF; 2 – DS-14 + +3% LZ-6/9 + 7% CP + 3% DF-11; 3 – DS-14 + 3% LZ-6/9 + 7% CP.

Table 25 gives results of radiometric determinations of corrosion of steel at a temperature of the oil of 200°C. It is clear that a difference in temperatures of decomposition (splitting of phosphorus) of triphenyl phosphite and tricresyl phosphite had an effect on the effectiveness of the anticorrosive action of these compounds in composition and with the chemically active mixture of counterseizing components: tricresyl phosphate did not give any anticorrosive effect, where triphenyl phosphate provided a sharp lowering of the corrosion [255].

Table 25. Comparative anticorrosive effectiveness of phosphorus-containing compounds.

Test sample	Corrosion of steel for 6 h, imp/min
Oil DS-14	32
DS-14 + 3% LZ-6/9 + 7% chlorinated paraffin . .	1648
The same + 5% tricresyl phosphate	1832
The same + 0.5% triphenyl phosphite	80

The absence of anticorrosive action with the application of tricresyl phosphate apparently, can be explained also by the fact that, as is shown in works [227, 228], the tricresyl phosphate in interaction with steel forms iron phosphate and not iron phosphide. If one were to use phosphorus-containing anticorrosive components in composition with the chemically most active counterseizing additives, then it is possible to use chemical compounds earlier rejected because of high corrosional aggressiveness.

Investigation of Chemical Activity of Counterseizing Additives to Oils Temperatures of 200-600°C

At high specific pressures on separate sections of the lubricated rubbing surfaces of heavily loaded mechanisms there appear local flashes of high temperatures (up to melting points of the metal) in the zone of contact of the metal with the oil [174].

The usually used determination of comparative chemical activity of different counterseizing additives with respect to steel and other metals at temperatures of the oil up to 250°C [165, 222, 258, 262] does not always correctly reflect the property of counterseizing additives. In separate cases with smaller reactivity of the additive A as compared to additive B under conditions of temperatures of the oil up to 250°C with a temperature rise its reactivity more sharply increases than for additive B, and at high temperatures the reactivity of additive A appears is larger than for additive B [213].

Thus, to investigate the mechanism of action and estimate the effectiveness of counterseizing additives to oils it is necessary to determine their chemical activity (reactivity) at different high temperatures in the zone of contact of metal with the oil under conditions of preserving the low temperature of the oil in volume.

To determine the speed of reaction of the interaction of counterseizing additives with metals at different temperatures in the zone of contact of the surface of metal with oil (up to 600°C) and temperature of the oil in volume of not over 100°C Barcroft [213] used an apparatus with pulse heating by electrical current of a wire of assigned metal. During the test the change of resistance of the wire due to interaction of the metal with the counterseizing additive is measured. Barcroft proceeded from the concept that the surface of the wire all along its length equally reacts with the investigated additive and that layer of surface of metal of wire, modified due to the reaction of interaction with the additive possesses considerably greater electrical resistance than that of the constant metals, which permits determining the decrease in diameter of the wire by the change in its resistance.

According to the results of experimental investigations of the reaction of interaction of counterseizing additives with wires of stainless steel,^{3} soft steel, pure iron, silver and copper at temperatures of their surface in the zone of contact with the oil which contained the additive from 100° to 600°C, Barcroft determined the speed of reaction of interaction of the additive with the metal at a given temperature from the equation

$$\ln K = -\frac{E}{RT} + \mathrm{const},$$

here K is the formation rate of the modified layer of metal during interaction of the additive with the metal, Å/min; E is the activation energy.

According to the obtained experimental data, the author plotted curves of the dependence of reaction speed of interaction of the additive with metal on the temperature in coordinates ln K – 1/T, where T is expressed in °K.

In these coordinates the obtained curves for all additives except phosphorus-containing additives were straight lines.

Typical results obtained by Barcroft during the investigation of counterseizing additives introduced into white medicinal oil are shown in Fig. 80. From the figure it is clear that the comparative reactivity for sulphurized oil is considerably higher than for dibenzyl disulfide in the whole range of temperatures up to 600°C, which provides its greater counterseizing effectiveness according to data of tests for gear reduction (4000 r/min; temperature of oil, 70°C, content of additives in white medicinal oil 0.5% wt. sulfur) given in Table 26.

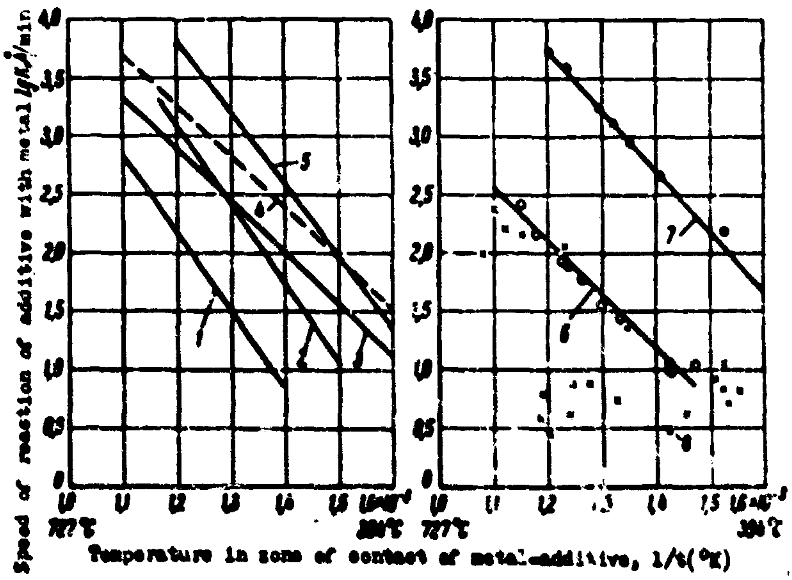

Fig. 80. Influence of temperature of wire surface on stainless steel on the speed of interaction of counterseizing additives with steel: 1 – dibenzyl disulfide (0.5 wt. % of sulfur); 2 – sulphurized oil (0.5 wt. % of sulfur); 3 – 8% chlorinated paraffin (3.2 wt. % of chlorine); 4 – 16% chlorinated paraffin (6.4% wt. % chlorine); 5 – dibenzyl disulfide + + chlorinated paraffin (0.5 wt. % of sulfur + + 3.2 wt. % of chlorine); 6 – zinc alkyl aryl dithiophosphate (0.5 wt. % of sulfur); 7 – zinc dialkyl dithiophosphate (0.5 wt. % of sulfur); 8 – tritolyl phosphate (0.5 wt. % of phosphorus)

Table 26. Results of bench tests of counterseizing effectiveness of sulfur-containing additives on gear reduction.

Tested oil	Load at which there appeared seizings and jammings, kg
White medicinal oil without additive	17,2
The same oil + additive of sulphurized oil	36,3
The same oil + dibenzyl disulfide	29,5

From Fig. 80 one can also see that a composition of dibenzyl disulfide and chlorinated paraffin possesses considerably greater reactivity than that of each of these additives separately, and at high temperatures even greater than 16% chlorinated paraffin. It is interesting to note that in the use of a composition of dibenzyl disulfide with chlorinated paraffin, X-ray diffraction analysis showed the presence on the surface of steel as a reaction product of the interaction of steel with a composition of additives of only iron chloride, but iron sulfide was absent. Barcroft notes that the correctness of the point of view Prutton and coauthors [165] is thereby confirmed about the fact that the increase set by them of counterseizing effectiveness during mixing of chlorine-containing additives with sulfur-containing additives is explained by the increase in formation rate of pliable iron chloride on the surface of the steel.

Special attention is drawn to results obtained by Barcroft in the investigation of phosphorus-containing counterseizing additives: it is clear that the temperature rise did not cause the increase in speed of reaction of the tritolyl phosphate with steel. The author notes that, apparently, the thin layer of products of reaction of phosphorus with the steel (500 Å or less) is sufficient for the blocking of further development of the reaction. X-ray diffraction analysis showed that the product of reaction was iron phosphide. Barcroft assumed that good results, obtained under conditions of exploitation with the application of oils with phosphorus-containing counterseizing additives, are explained by the fact that phosphide films are very durable, resist abrasion well and therefore are preserved on rubbing surfaces for a long time.

In connection with widespread point of view during the last few years about the fact that counterseizing effectiveness of zinc dialkyl dithiophosphate depends on the character of the organic radical, Barcroft investigated the comparative reactivity of zinc dialkl- and aryl alkyl dithiophosphates contained in white medicinal oil in the quantity of 0.5 wt. % of sulfur. As can be seen from Fig. 80, the shown zinc dithiophosphates possessed an absolutely different reactivity.

Campbell and Grunberg [147] used the wire instrument developed Barcroft [213] in combination with the use of sulfur-containing additives labeled by the isotope S^{35}. Labeled additives were introduced into 40 ml of liquid paraffin in a quantity of 0.5 wt. % sulfur, and the activity of the sample was from 10 to 100 μCi. Other additives were introduced into the solution in a quantity of 0.5 wt. % chlorine or phosphorus.

There is investigated the interaction with stainless steel, soft steel, iron, copper and bronze, at temperatures of the surface of the wire in the zone of contact with the oil from 100° to 600°C, of elementary sulfur and dibenzyl disulfide, labeled by isotope S^{35}, and composition of these additives with tributyl phosphite tricresyl phosphate and chlorinated paraffin.

The quantity of labeled additive reacting with the surface of the wire during the time of the experiment was determined by means of location of electrodes with the wire (after washing in benzene) into the lead chamber with an end-window Geiger counter. First the radioactivity of the electrodes together with the wire was measured and then the wire was removed and the radioactivity on the electrodes was measured. The difference in the counting rate reflected the quantity of labeled additive reacting with the surface of the wire. With the help of radioautographs standardization was carried out, allowing the evaluating of data of radiometric measurements in quantities of labeled additive expressed in grams per square centimeter.

The greatest interest in the investigations of Campbell and

Grunberg [147] is in their sharp lowering of the quantity of film formed by sulfur-containing additives in the presence of phosphorus-containing compounds and chlorinated paraffin. Thus elementary sulfur formed a film on the surface of the steel with a thickness of 300 Å at 400°C and 1200 Å at 600°C and in the presence of tributyl phosphite the formation of a film of sulfur was practically not observed. The interaction of dibenzyl disulfide with steel was effected to a lesser degree by the introduction of tributyl phosphite. Tricresyl phosphate to a lesser degree suppressed the interaction of sulfur-containing additives with steel.

We developed an experimental apparatus for the determination of chemical activity of counterseizing additives to oils with respect to different metals at temperatures in the zone of contact of the surface of metal with oil from 200 to 600°C and a temperature of the oil in volume not over 100°C. To determine the chemical activity of the investigated additives there is used radioactive wire of assigned metal [82, 263]. On this apparatus it is also possible to conduct investigations with the help of methods proposed by Barcroft [213] and Campbell and Grunberg [147].

Figure 81 shows the working unit of the apparatus, which constitutes a beaker 2 of stainless steel with the oil to be investigated. The beaker is closed by a cover of insulating material 6, in the cover there are fastened holders 5 of radioactive wire 3 0.3 mm in diameter and having an effective length of 25 mm thermocouple 4 and two mixers 7, rotated by an electric motor 8. The beaker is screwed into the bath 1 with running water for maintaining the temperature of the tested oil at the assigned limits.

The source of current fed by pulses to the wire is a storage battery (24 V). The pulse character of the current supply is provided by a mechanical chopper, which is rotated by an electric motor using direct current from a rectifier [VSA-6M] (BCA-6M). The chopper provides a supply of current pulses for 4 μs with a pause of 40 μs at a speed of rotation of the collector of 675 r/min, i.e, the ratio of the time of heating and cooling of the wire of 1:10 is sustained.

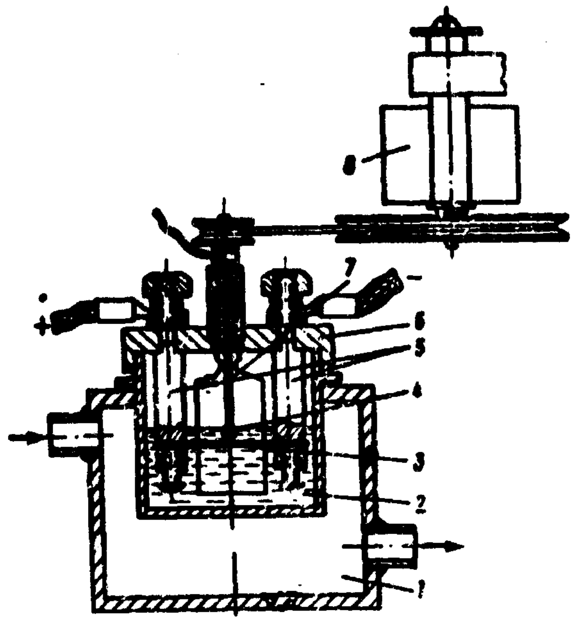

Fig. 81. Working unit of the apparatus: 1 - cooling bath; 2 - beaker of stainless steel into which the tested oil with the additive is filled; 3 - radioactive wire (∅ 0.3 mm, ℓ = 25 mm); 4 - thermocouple; 5 - holders; 6 - cover of insulating material; 7 - mixer; 8 - electric motor.

The revolutions of the electric motor, which rotates the collector and the magnitude of the current fed to the wire from the storage battery are regulated by rheostats. Short-duration current pulses fed to the wire provide bursts of assigned temperature in the zone of contact of the surface of the wire with the oil. The electrical circuit of the apparatus is shown in Fig. 82.

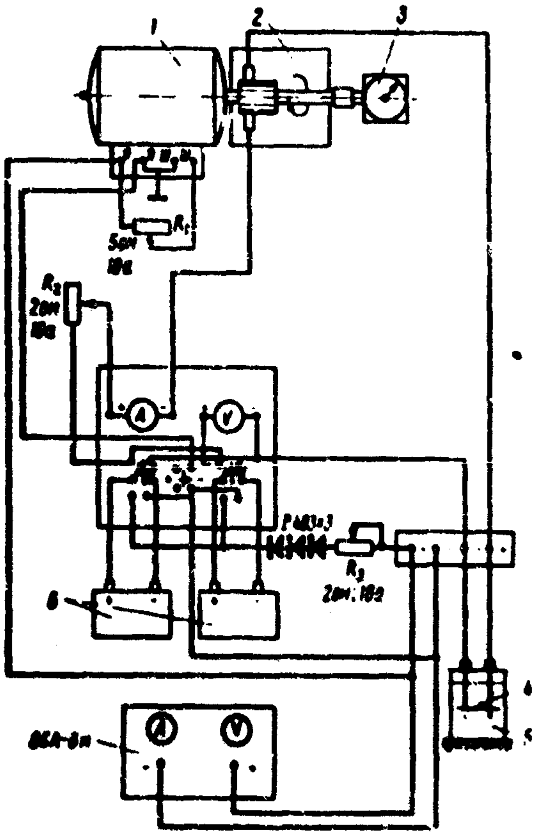

Fig. 82. Electrical circuit of the apparatus with mechanical chopper: 1 - direct current electric motor; 2 - mechanical chopper; 3 - tachometer; 4 - wire ∅ 0.3 mm; 5 - investigated oil product; 6 - storage batteries of 24 V.

There has been also developed a variant of the apparatus excluding need to use a mechanical chopper and storage battery in connection with the application of alternating voltage of the network with a cutoff of one of the half-periods. The electrical circuit of this variant of the apparatus is shown in Fig. 83. Due to the large inductance of dispersion of the output transformer pulses passing through diodes have smaller duration than the half-period of current in the network (7-8 ms instead of 10) and a pause of 12 ms, which increases the total amount of pulses per unit time (as compared to the variant of the apparatus with a mechanical chopper), i.e., there are provided more frequent bursts of high temperatures in the zone of contact of the surface of radioactive wire with the tested oil.

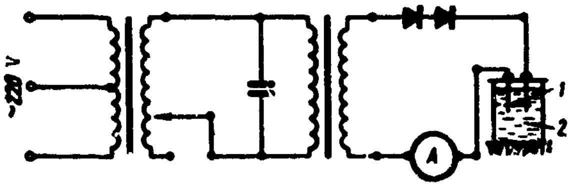

Fig. 83. Electrical circuit of the apparatus without a mechanical chopper; 1 – wire ∅ 0.3 mm; 2 – investigated oil product.

The temperature of the wire was set by the calibration graph T = = f(I). In order to obtain initial data for construction of this graph, the nonradioactive wire, fastened in the holders is submerged into the transparent cuvette with a liquid of a known boiling point. The cuvette is illuminated by an electrical tube in order to provide observation of the state of liquid in the zone of contact of it with the surface of wire by means of an eyepiece of a microscope. Calibriation is conducted by putting the wire into the following liquids: isooctane ($T_{b.p.}$ = 99.3°C), α-methyl naphthalene ($T_{b.p.}$ = = 229°C) and dibutyl phthalate ($T_{b.p.}$ = 340°C). Thermal conditions of these liquids are close to the thermal conduction of mineral oil.

The current passed by pulses through the wire with the help of a rheostat was increased until there appeared indicators of the beginning boiling of the given liquid on the surface of the wire (separate vials of gas), i.e., until the surface of the wire reached a temperature necessary for boiling of the given liquid. Thus, the magnitudes of current corresponding to boiling temperatures of the liquids indicated above are determined.

For calibration in a range of higher temperatures the nonradioactive wire, secured in the holders, was cut and in a clearance (equal to 0.1-0.15 mm) there was soldered alternately metals and alloys with a preliminarily measured melting point. There were used the following metals and alloys: tin, lead, zinc and silver solder. The wire was put into the transparent cuvette with mineral oil and through the wire by pulses a current was passed, which with the help of a rheostat increased to such values when the metal, filling the clearance in the wire, started to be melted (wire was broken). Thus the values of current corresponding to the melting point of the indicated metals were determined.

A graph of the dependence of temperature of the surface of wire on the value pulse current passed through it was constructed from values of magnitudes of current obtained by both methods. As can be seen from the graph shown in Fig. 84, in the range of temperatures from 100° to 620°C with the conducted calibration there was obtained linear dependence. The investigated oil (30 cm^3) with a counterseizing additive was filled in the working unit of the apparatus in which the radioactive steel wire, activated by neutrons in a nuclear reactor, was secured.

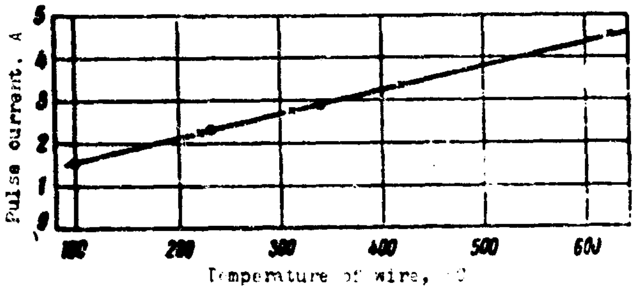

Fig. 84. Calibration graph of the dependence of temperature of the surface of wire on the magnitude of pulse current passed through it: ● – boiling point of isooctane, α-methylnaphthalene and dibutyl phthalate; x – melting point of tin, lead, zinc and silver solder.

Rheostats set the assigned values of the current and the number of revolutions of the collector of the apparatus and the assigned temperature in the zone of contact of the oil with the surface of the wire was created. With help of the cooling system the assigned temperature of the oil in volume was set. After 5 minutes of work in the assigned conditions the apparatus was turned off, the cover with holders of the radioactive wire and mixers was removed, and the beaker with the tested oil was placed into the apparatus with a scintillation counter for measurement of radioactivity.

With measurement of radioactivity of the oil there was determined the quantity of radioactive metal which passed into the oil in the process of interaction of chemically active counterseizing additive with the surface of the metal. Each experiment was repeated not less then 6-8 times. To convert the results of radiometric determinations into weight indices the method of standardization was used. The developed method provided fully satisfactory reproducibility of results of the investigations.

Figure 85 shows the results of the investigation of oil DS-11 with different counterseizing additives and their compositions. It is clear that the chemical activity of the investigated additives with an increase in temperatures was changed differently. It is necessary to note that the introduction of triphenyl phosphite into oil DS-11 with 7% chlorinated paraffin [254-256] provided an anticorrosive effect in the whole range of investigated temperatures.

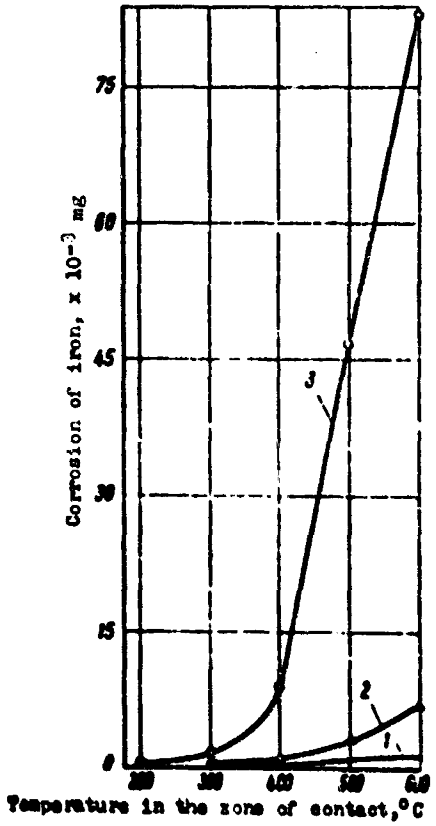

Fig. 85. Change in chemical activity of certain counterseizing additives and compositions with an increase in temperatures on the surface of steel wire: 1 - DS-11 + + 3% LZ-6/9; 2 - DS-11 + 7% CP + 0.5% TPP; 3 - DS-11 + + 7% CP.

It should be noted that in the last works of Sakurai and Sato [245], and also Rounds [246] it is established that results of the investigation of chemical activity of counterseizing additives under conditions of static tests can in a number case differ from data obtained under conditions of dynamic tests.

Thus, Sakurai and Sato [245], using a wire instrument and the method of investigation of chemical activity of counterseizing additives developed by Barcroft [213], established that with identical chemical activity of the sulfur-containing and chlorine-containing additives in the whole range of temperatures (100-600°C) these additives according to data of test in dynamic conditions, possessed different counterseizing effectiveness.

Investigation of the Mechanism of Action of Molybdenum-Organic Additives to Oils

In recent years as a lubricating material there has widely been used molybdenum disulfide [191, 264], able to provide counterseizing action in the range of temperatures (-75)-(+540)°C. Methods have been published for obtaining oil soluble molybdenum – sulfur-containing compounds decomposed at high contact temperatures on rubbing surfaces with separation of solid molybdenum disulfide. Application is found of oil-soluble molybdenum-organic complex compounds in the form of molybdenum blue reacting with the sulfurous component of the additive under conditions of high contact temperatures on rubbing surfaces with the formation molybdenum sulfide compounds. Is shown that molybdenum blue in pure form (without a sulfurous component) also possesses considerable counterseizing properties.

The stable form of molybdenum blue constitutes a complex compound of oxides of penta- and hexavalent molybdenum, including also the compound of phosphorus. The approximate formula of this complex compound can be represented in the following form:

$$H_3PO_4(MoO_2 \cdot 4MoO_3)_2 \cdot 4H_2O.$$

The chemical composition and physical and chemical properties of molybdenum blue depend on conditions of its obtaining [191]. With the replacement of water of hydration in the composition of a molecule of molybdenum blue by an organic compound it becomes oil-soluble.

We used the method of radioactive tracers to study the mechanism of action of oil-soluble molybdenum blue with the application of it as an additive to oils both in pure form and in composition with the sulfur-containing additive (dibenzyl disulfide). For the investigations there were used molybdenum blue labeled by isotopes P^{32} and C^{14} which was synthesized with the application as reagents of $Na_2HP^{32}O_4$ and $C_4H_9C^{14}H_2OH$ respectively, and also dibenzyl disulfide, labeled by S^{35}, with synthesis of which elementary sulfur containing S^{35} was used.

Labeled additives – 3.6% molybdenum blue and 3% dibenzyl disulfide – were dissolved in base oil (dioctyl sebacate) and their interaction with the surface of steel at different temperatures of the oil was studied. Investigations were conducted on the Pinkevich apparatus with steel disks at temperatures of the oil of 80°, 110° and 140°C. The quantity of labeled additive entering into interaction with the surface of steel was determined with the help of radiometric measurements by the usual method [105, 106].

Figure 86, for example, gives results of experiments at a temperature of the oil of 140°C. Plotted along the axis of the ordinates are the quantities of additive on the surface steel calculated according to measurements of intensity of radiations of isotopes P^{32} and C^{14}.

It was determined that with a temperature rise there is increased the quantity of additive on the surface of the steel revealed by radiation of isotopes P^{32} and C^{14}, and also that with a temperature increase the speed of interaction of the additive with the steel is increased.

Table 27 gives ratios between quantities of the additive on the surface steel calculated according to measurements of intensity of radiation of isotopes P^{32} and C^{14} during the carrying out of experiments under conditions of different temperatures of the oil. From Table 27 it is clear that the ratios between quantities of the additive on steel calculated by radiation of isotopes C^{14} and P^{32}, are preserved approximately identical at all temperatures. The numerical value of these ratios (approximately 1:6) permits assuming that in the complex compound of molybdenum blue there is contained about 15% aniline alcohol. The indicated constancy of the ratio between the quantity of carbon and phosphorus on the surface of steel indicates that with the interaction of molybdenum blue with steel, on the surface of the latter a film consisting of molecules of molybdenum blue will be formed.

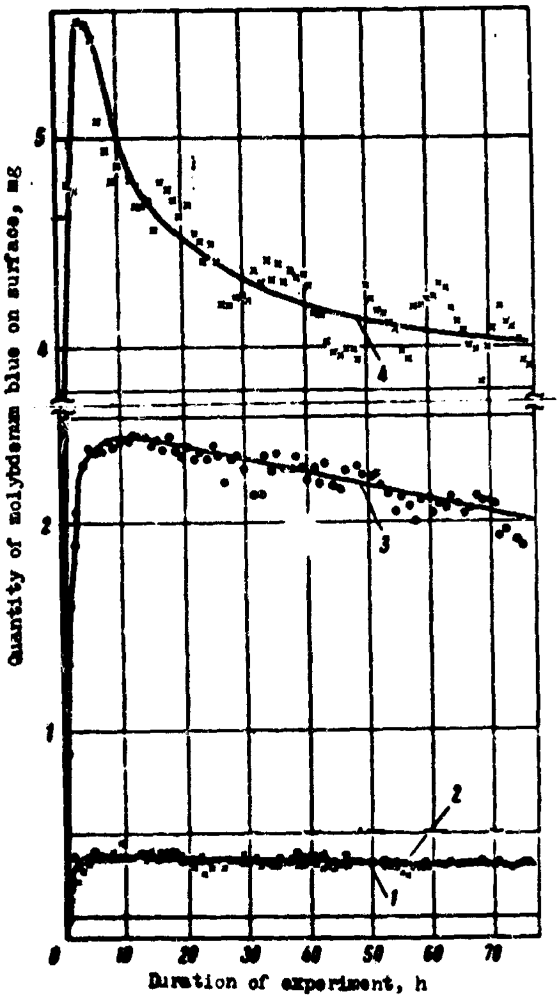

Fig. 86. Kinetics of the interaction of molybdenum blue (3.6% in dioctyl sebacate) and its mixture with dibenzyl disulfide (3%) with the surface of steel. Temperature of dioctyl sebacate, 140°C: 1 – DOS + molydenum blue (C^{14}) + DBDS; 2 – DOS + + molybdenum blue (C^{14}); 3 – DOS + molydenum blue (P^{32}); 4 – DOS + + molybdenum blue (P^{32}) + DBDS.

Table 27. Ratios between quantities of the additive of molybdenum blue on the surface of steel calculated by radiation of isotopes C^{14} and P^{32}.

Duration of experiment, h	Quantity of molybdenum blue on the surface of steel calculated by radiation of isotope P^{32} and C^{14} at a temperature of the oil°C								
	80			110			140		
	P^{32}	C^{14}	P^{32}/C^{14}	P^{32}	C^{14}	P^{32}/C^{14}	P^{32}	C^{14}	P^{32}/C^{14}
10	0.110	0.022	1:5.00	0.720	0.110	1:6.55	2.400	0.390	1:6.16
20	0.150	0.038	1:3.94	0.880	0.126	1:7.23	2.100	0.340	1:6.21
30	0.320	0.045	1:7.11	0.925	0.119	1:7.76	2.300	0.360	1:6.20
Mean			1:6.02			1:7.19			1:6.19

Figure 87 gives results of experiments at 140°C with dibenzyl disulfide, labeled by isotope S^{35}, introduced into dioctyl sebacate and into a solution of molybdenum blue in dioctyl sebacate. It is clear that in the presence of molybdenum blue the quantity of sulfur on the steel surface increases.

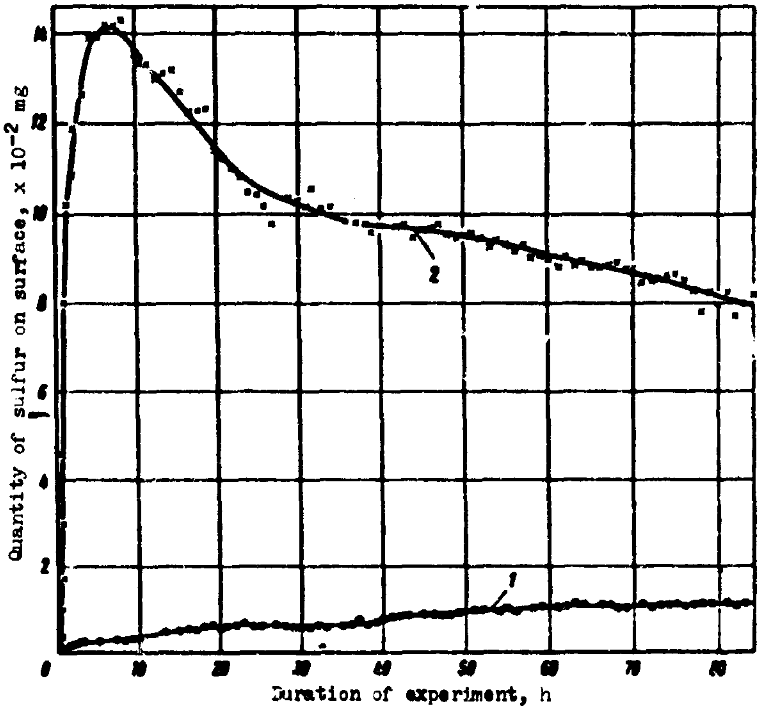

Fig. 87. Kinetics of the interaction of dibenzyl disulfide (3% in dioctyl sebacate) and its mixture with molybdenum blue (3.6%) with the surface of steel. Temperature of dioctyl sebacate, 140°C: 1 - oil DOS + DBDS (S^{35}); 2 - DOS + molybdenum blue + DBDS (S^{35}).

From Fig. 86 it is clear that in the presence of dibenzyl disulfide the quantity of molybdenum blue on the steel surface, calculated by radiation of isotope P^{32}, sharply increases, whereas according to data of the measurement of radiation of isotope C^{14} such an effect is not observed.

The increase in the quantity of phosphorus and sulfur on the steel surface with joint application of molybdenum blue and dibenzyl disulfide indicates that these compounds in the investigated interval of temperatures enter into a reaction with the formation of molybdenum sulfide compounds which create a protective film on the steel surface. The complex compound of molybdenum blue then, apparently, disintegrates, and the alcohol labeled by isotope C^{14}, is split off and does not participate in the formation of the protective film.

The established mutual influence of molybdenum blue and sulfurous component on their interaction with steel agreed well with the conducted tests on the four-ball friction machine: the molybdenum blue possessed effective counterseizing action, which was strengthened with an increase in its concentration in the oil. In a combination of molybdenum blue with a sulfurous component the effectiveness of its action increased [264].

Investigation of the Influence of Counterseizing Additives on Wear Under Small Loads

The chemical interaction of rubbing surfaces with counterseizing additives which prevent and reduce seizings and jammings under conditions of high loads and contact temperatures, can under small and moderate loads cause chemical wear, which in certain cases considerably exceeds the wear during operation with oils without additives. To study the influence of chemical activity of counterseizing additives on wear under small loads there have been developed radioactive tracer methods of the investigation of these additives, on friction machines [254, 255, 265]. The construction of one of the machines [254] is shown in Fig. 88. The end rubbing surface of the working cup 3 was activated by insertions of Co^{60}. The measuring circuit of radioactivity of oil in the bath 2 with the help of a scintillation counter is shown in Fig. 89. Peculiarities of the machine are the use of small quantities of tested oils (up to 10 cm^3) and the measurement of radioactivity of the entire oil. The machine is supplied with heating can operate under loads up to 80 kg/cm^2, the number of revolutions up to 1000 per minute and temperatures of the oil up to 250°C.

With the use of a nonradioactive cup and additives labeled by radioactive isotopes of basic components, it is possible to establish the kinetics of interaction of additives with surfaces of metals and of the formation by them of films on surfaces under conditions of friction by conducting measurements of the quantity of film by the radiation of labeled components of additives according to the diagram shown in Fig. 90.

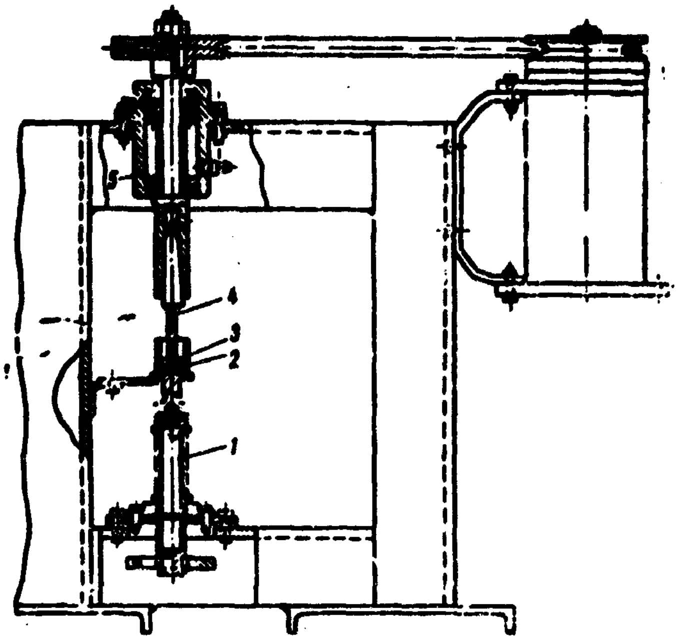

Fig. 88. Diagram of the friction machine for radioactive tracer investigation of the influence of chemical activity of counterseizing additives on the wear of rubbing surfaces under small loads: 1 – mechanism of load; 2 – bath; 3 – working cup; 4 – drive shaft; 5 – centering unit.

For example, Fig. 91 gives results of the investigation of oil MT-16 with counterseizing additives on the examined friction machine with the use of dibenzyl disulfide, labeled by isotope S^{35}. One can see the growth in wear of rubbing surfaces in operation with an oil with counterseizing additives under conditions of used low loads and temperatures of oil (10 kg/cm^2, 150°C). One can also see that in the presence of chlorinated paraffin the quantity of sulfide film on the rubbing surface descends, and the speed of wear of the rubbing surfaces increases.

It should be noted that Barcroft and Daniel [266], in conducting recently a test of oils with counterseizing additives (labeled by isotopes S^{35}) and their compositions in hypoidal transmissions in bench test conditions, revealed that under high loads in the presence of 10% chlorinated paraffin the quantity of film recorded on the surface of the steel gear teeth by β-radiation of S^{35} not only does not decrease but even increases.

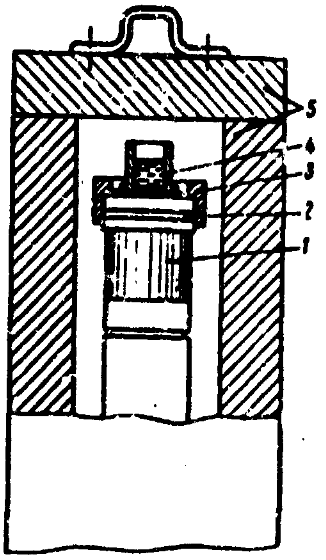

Fig. 89. Measuring diagram of radioactivity of oil for the determination of speed of wear: 1 - electron multiplier phototube; 2 - NaJ crystal of scintillation counter; 3 - support-stop of the bath on the crystal; 4 - bath of the friction machine; 5 - lead shielding.

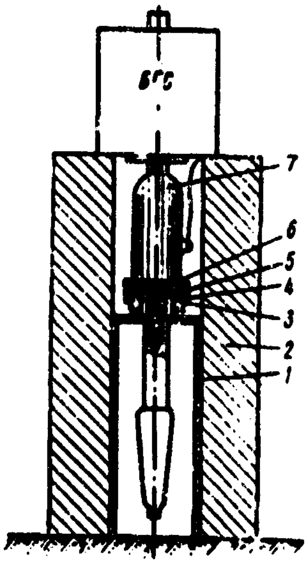

Fig. 90. Measuring diagram of the quantity of labeled component of additive on the rubbing surface according to its radiation: 1 - support; 2 - lead shielding; 3 - outer aluminum shield; 4 - rubber support; 5 - working cup of the friction machine; 6 - internal aluminum shield; 7 - end-window Geiger counter MST-17.

In the test of the composition of the sulfur-containing additive (sulphurized oil) and 1% organic phosphorus compound it is established [266] that at comparatively lower temperatures on the surface of the gear teeth there is revealed more films formed by phosphorus and at higher temperatures, films formed by sulfur.

The unit of friction of other machine [265] consisted of, as one can see from Fig. 92a and b, hollow cast-iron cylinders touching on the ends, one of which (upper, external and internal diameters are 16 and 10 mm respectively) is activated by three insertions of Co^{60}. The lower cylinder revolved at a speed of 600 r/min. The load was carried out owing to the weight of the upper unit sliding along the cylindrical guide supports.

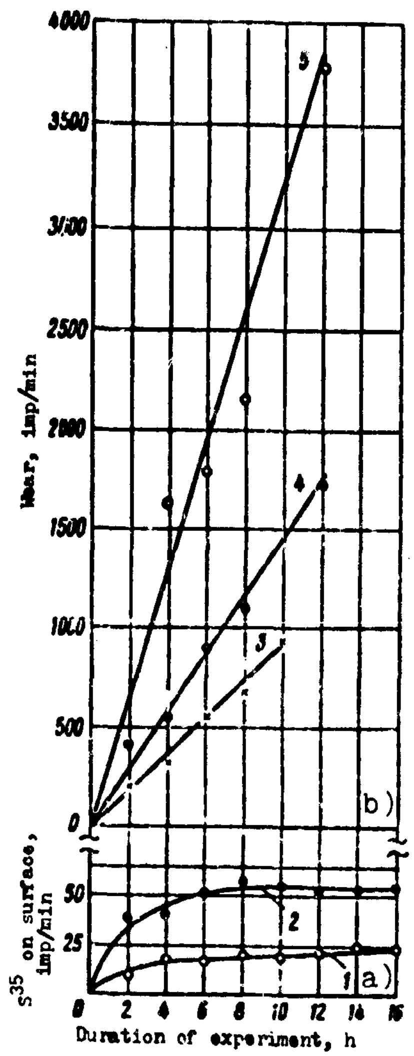

Fig. 91. Kinetics of the interaction of labeled dibenzyl disulfide with rubbing surfaces a) and results of the investigation of wear of rubbing surfaces b) during work with oil MT-16 with counterseizing additives: 1, 5 – MT-16 + 3% dibenzyl disulfide + 7% chlorinated paraffin; 2, 4 – MT-16 + + 3% dibenzyl disulfide; 3 – oil MT-16 without additives.

Before the beginning of the test the loading device together with the upper cylinder were removed, and on the right guide support, as was shown in Fig. 92c, there was set a lap – metallic sector with a centering bushing. On the lower end face of the sector with the help of clamp laths there was fastened a removable small emery cloth. Lapping was carried out manually by a reciprocating displacement of the lap about the end face of the lower cylinder under constant load owing to the intrinsic weight of the lap. Upon completion of the lapping the lap was removed; then the rubbing surface and cavity of the cylinder were washed by gasoline, after which their radioactivity was measured in order to be convinced that with the help of lapping and washing radioactive products of wear passing over during the preceding experiment to the lower rubbing are removed completely.

Into the cavity of the lower cylinder from the pipette there was introduced 0.3 cm^3 of the tested oil (this provided the presence of an oil film on the rubbing surfaces), after which with the help of an end-window counter the initial radioactivity of the oil was measured. Installed on the machine was a loading device, and a test was conducted for 1 hour. Upon completion of the test the loading device together with the upper cylinder were removed and on the right guide support, as was shown in Fig. 92d, there was installed with the help of a bushing, a holder for a counter and extension unit of the radiometric apparatus. The counter was fixed with respect to the rubbing surface of the lower cylinder.

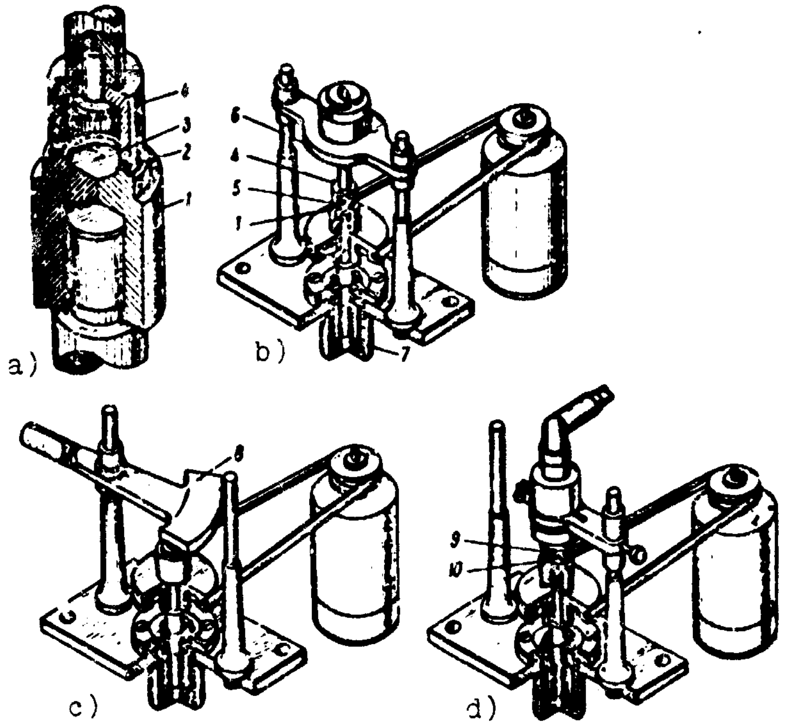

Fig. 92. Diagram of the friction machine for the radioactive tracer investigation of wear of rubbing surfaces during a test of oils with counterseizing additives under conditions of small loads: a) friction unit of the machine; b) friction machine during carrying out of the oil test; c) friction machine during carrying out of lapping of working end face of lower nonradioactive rubbing specimen; d) friction machine during measurement of radioactivity on lower specimen; 1 - nonradioactive rubbing specimen; 2 - insertion of Co^{60}; 3 - oil chamber; 4 - radioactive rubbing specimen; 5 - tested oil; 6 - loading device; 7 - centering device; 8 - lap; 9 - Geiger counter; 10 - aluminum filter.

The following are characteristics of the developed method of the test: measurement of radioactivity of the entire working oil with simultaneous calculation of the quantity of radioactive metal converted into a conjugate nonradioactive part; lapping of nonradioactive rubbing part, which permits avoiding the need to work in the rubbing surfaces before every test; the periodic carrying out of control experiments on standard oil, especially after a test of oils with chemically active additives.

From Table 28 it is clear that the introduction into oil DS-14 of counterseizing additives sharply increased the wear of rubbing surfaces. The application of these additives in composition with trifenyl phosphate (leading, as was shown above, to the removal of corrosion) provided wear of rubbing surfaces under small loads practically on the level of wear which was observed during work with oil without additives.

Table 28. Results of radioactive tracer wear tests of oil with counterseizing additives on the friction machine.

Oil	Mean value of wear, imp/min
DS-14	660
DS-14 + 3% LZ-6/9 + 7% chlorinated paraffin	1920
The same oil with additives + 0.5% triphenyl phosphate	840

Thus it is experimentally shown that the application of certain phosphorus-containing compounds as anticorrosive components in compositions with counterseizing additives not only sharply reduces corrosion but also provides lowering of the chemical wear of rubbing surfaces under small loads.

Recently for investigation of the influence of chemical activity of counterseizing additives on wear, Taylor and Wilde [267] used a friction machine whose diagram is shown in Fig. 93. The friction unit of the machine was a steel[3] roller with a diameter of 39 mm with two cylindrical belts sliding along the cylindrical surface of a steel[3] disk 60 mm in diameter.

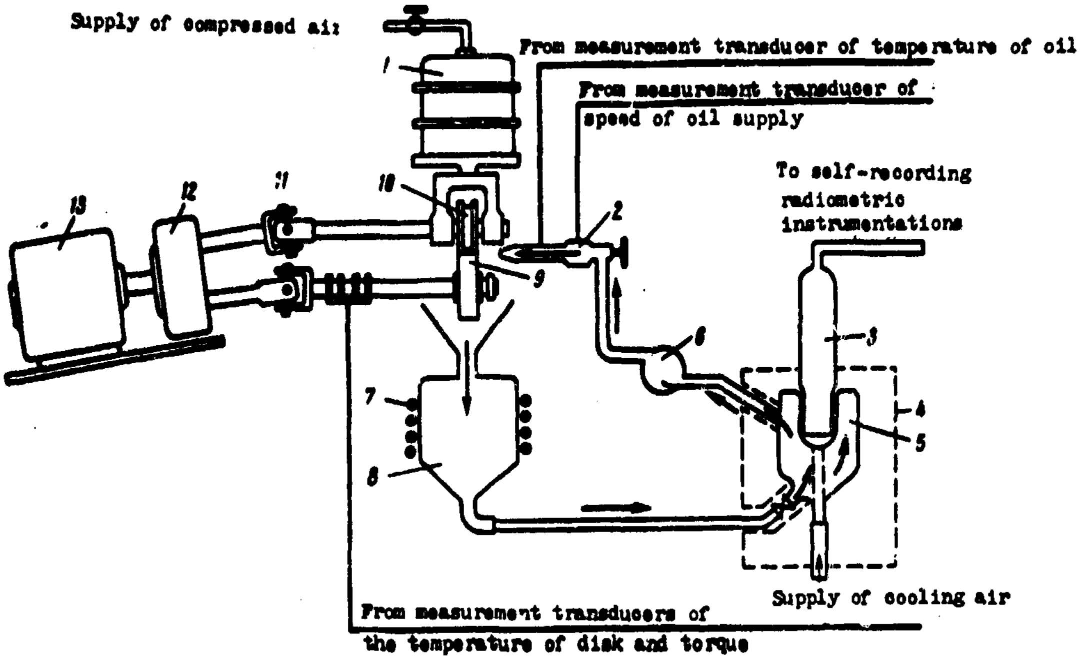

Fig. 93. Diagram of the experimental apparatus for determination of wear during a test of oils with counterseizing additives: 1 – power cylinders of pneumatic loading unit; 2 – adjustable lubricator; 3 – scintillation counter; 4 – lead chamber; 5 – measuring vessel; 6 – oil pump: 7 – electroheating; 8 – oil tank; 9 – disk; 10 – radioactive roller; 11 – Hooke hinges; 12 – reductor; 13 – electric drive motor.

The roller and disk were rotated by an electric motor through a reduction gear and Hooke's hinges. With such a system it is possible to set the speed of slip of the roller along the disk from 0.35 to 1.24 m/s. The friction unit was loaded with the help of a pneumatic system. The roller was activated by irradiation by neutrons in a nuclear reactor.

Into the zone of contact of the roller with a disk of lubricator there was fed a strictly controlled quantity of oil – 0.8 ℓ/min. The speed of wear was estimated by the increase in radioactivity of the circulating oil with the help of a scintillation counter and self-recording equipment. There was also estimated the transfer of metal of the radioactive roller to the cylindrical surface of the disk by means of removal of radioautographs from the latter. With this the quantity of transferred metal and character of transfer were determined.

Taylor and Wilde [267] especially note that with the development of the method of tests there was established the expediency of the application of rollers and disks with the assigned cleanness of the surface, which excluded observed cases of the increase in temperature of the oil on the first stage of tests and the lowering of the load of jamming with application of rollers and disks with large dimensions of roughnesses. Transducers which allowed the recording of coefficients of friction with the help of an oscillograph, were installed on the shaft of the disk.

A test was conducted with a step change of the loads: first there was carried out running in for 30 minutes on a load of 7000 kg/cm^2 per Hz. The load was increased further to 10,500 kg/cm^2 for 20 minutes and then every other 20 minutes by 700 kg/cm^2 up to appearance of seizing and jammings.

In the process of the tests temperatures of the oil and surfaces of the roller and disk were periodically recorded. There were also recorded values of the coefficients of friction. Experiments were conducted at temperatures of the oil from 70° to 120°C.

Figure 94, for example, shows results of tests of one of the oils with a counterseizing additive. From the figure it is clear that wear of the surfaces of friction depended on their temperature.

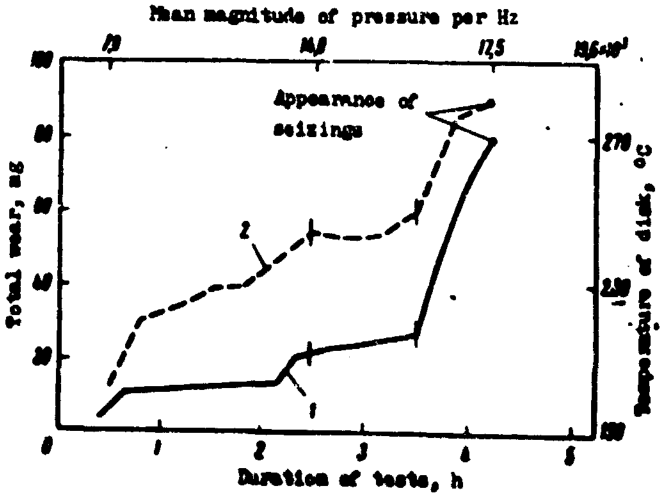

Fig. 94. Change in temperature of the rubbing surfaces (2) and wear (1) during a test of oil with a counterseizing additive under conditions of a step increase of loads.

Figure 95 gives typical results of tests of three oils with counterseizing additives. It is clear that it is possible to select such a composition of counterseizing additives (oil C) which will not only possess high counterseizing effectiveness but also provide low rate of wear.

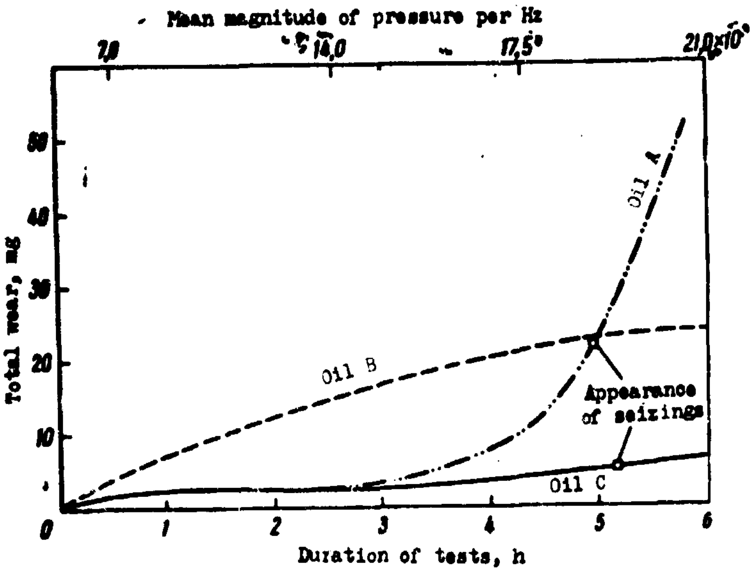

Fig. 95. Results of tests of three oils with counterseizing additives.

As researchers have noted during the last few years [188, 204, 268], the study of the influence of chemical activity of counterseizing additives on the rate of wear of rubbing surfaces is very important.

Footnotes

[1] In Fig. 76 the shaded field encompasses results of the determinations of anticorrosive effectiveness of a large quantity of different anticorrosice additives, not giving an effect in the composition with a chemically active mixture of counterseizing additives.

[2] Barium alkyl phenolate additive of formaldehyde condensation.

[3] Barcroft specially notes that with the use of different steels there were obtained identical characteristics of comparative reactivity of counterseizing additives in the investigated range of temperatures: the difference was in absolute values of reaction speeds. It is shown thereby that there is no need to investigate the comparative reactivity of counterseizing additives by the method developed by Barcroft certainly just with the help of a steel wire, which corresponds to the material of gears, in contact with which oil with these additives will work; but it is possible to use wire of any steel.

[4] Cemented steel with a hardness $R_c = 61$.

CHAPTER 6

CERTAIN PECULIARITIES OF WEAR OF AN INTERNAL COMBUSTION ENGINE WITH THE APPLICATION OF OILS WITH ADDITIVES

The solution to the most important national and economic problem for increasing the longevity of machines and mechanisms depend on the effectiveness of reducing wear. We examined how there has been developed the application of radioisotope methods in search of ways to reduce wear under conditions of the application of counterseizing additives to oils for heavily loaded units of friction.

Resolution of the problem of combating wear of engines for the purpose of increasing their engine resource is an even more complex and urgent problem. Above we examined the application of radioisotope methods during the study of mechanism of action of additives to motor oils, which reduce the corrosive wear of the cylinder-piston group of internal combustion engines, the corrosion of antifriction alloys of bearings of engines and electroerosional wear. There have already been touched upon partially questions of the compatibility of additives of different functional action, the study of antagonism and synergism with the formulation of compositions of additives to motor oils. The experiment taking place in our country and abroad in recent years shows that the application of radioisotope methods of investigation considerably expand the possibility of experimenters during the study of complex effects manifested under conditions of the application of additives and composition of additives with multifunctional properties in internal combustion engines.

Thus recently with the development of additives to motor oils

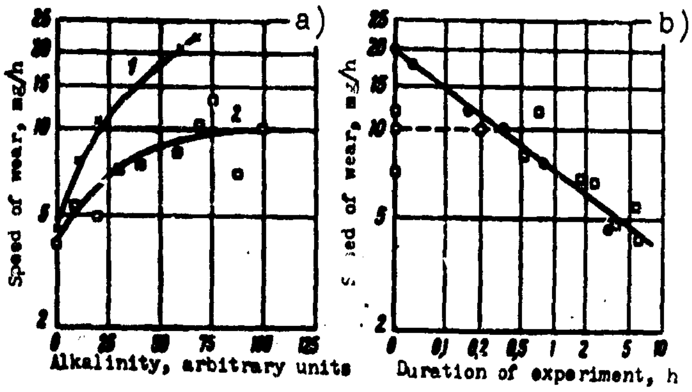

Fig. 96. Results of tests of a one-cylinder engine with a radioactive piston ring using oil with additives: 1 - neutralizing additive; 2 - combination of neutralizing and film-forming additives; ●——● - barium phenolate; □——□ - barium phenolate + barium sulfonate.

considerable attention was given to the selection of combinations of components which are able to provide both a neutralizing action and the formation of protective films on the rubbing parts of an engine. By experimental investigations it is shown that the combination of a neutralizing component with a protective one provides greater reduction in wear of an engine than the application of only a neutralizing component with the identical content of a metal of additive in the oil. Corresponding results obtained in the work Randall and coauthors [38] are shown in Fig. 96.

A one-cylinder carburetor engine with a radioactive upper compression piston ring operated in these conditions: 1200 r/min, full throttle valve, at a temperature of water cooling at the outlet 15°C and oil in the crankcase, 40°C. In the system of lubrication there was included a unit of measurement of radioactivity of the circulating oil with the help of a scintillation counter.

Figure 96a shows the change in speed of wear of the engine (mg of iron/h) during operation on oil with a neutralizing component (barium phenolate - curve 1) and on oil containing a neutralizing and protective component (barium phenolate + barium sulfonate - curve 2). It is clear that in proportion to the consumption of the neutralizing component the speed of wear of the engine increases in the first case (curve 1) continuously and in the second case (curve 2) up to full consumption of the neutralizing component, after which it remains approximately constant as a result of the action of the protective film created by the second component. The latter can be especially clearly seen from Fig. 96b on which the same data are plotted depending upon the alkalinity of the oil, which was changed in the process of operation of the engine (alkalinity reflects the consumption of the neutralizing component).

In the same work of Randall and coauthors [38] there was investigated the influence of many combinations of different additives – neutralizing, counterwear, counterseizing, antioxidant and others – on the wear of an engine, and it is shown that certain combinations provide the greatest counterwear effect. At the same time in certain cases there was established the rate increase of wear with the mixing of additives. The authors of these investigations did not examine and did not explain the indicated effects having extreme importance for the determination of the optimum structure of compositions of additives to motor oils.

An attempt to explain the cause of the increase in wear with the application of motor oils with certain additives is made in the work of Wakuri and coauthors [30]. By these investigations it is established that the application of high-alkali neutralizing additives in ship engines can under conditions of high thermal intensity cause increased wear.

Data of plant bench and running tests of engines showed that increased wear of piston rings (usual wear of rings of these engines did not exceed 1 mm for 1000 h) basically appeared in the period of breaking in and either occurred in all cylinders of every engine or in none of them. With this mainly the lower piston rings wore out. An analysis showed (Table 29) that such a phenomenon was observed during the use for breaking in of oils with high-alkali neutralizing additives. In the application of oils with additives, which authors

Table 29. Influence of additives to oils on the wear of piston rings of ship engines.

Operation of engine under conditions	Wear of engine			
	using oil with detergent additive	number of engines	using oil with high-alkaline neutralizing additive	quantity of engine
Plant breaking in on bench	Normal Increased	9 0	Normal Increased	1 8
Running plant breaking in tests	Normal Increased	2 0	Normal Increased	7 8

call detergent, increased wear was absent. It is necessary to stress that oils with high-alkali neutralizing additives after breaking in of an engine using an oil with a detergent additive did not cause increased wear.

Revealing such an effect, Wakuri and coauthors [30] conducted bench tests of oils with additives on a one-cylinder engine to study the mechanism of this phenomenon. They proceeded from the concept of the fact that the distinction in behavior of neutralizing and detergent additives can be affected by their nonidentical thermal stability. To check such an assumption there were tested oils with the indicated additives on a one-cylinder engine (with a diameter of the cylinder of 110 mm) at different temperatures of the piston: 160, 180 and 200°C. As can be seen from Fig. 97, an increase in temperature of the piston from 160° to 180°C caused a sharp increase in the speed of wear of the piston rings during operation on oil with a high-alkaline neutralizing additive, whereas on oil with a detergent additive the wear slightly increased only at a temperature of the piston of 200°C. Measurements of the coefficient of friction during tests for a one-cylinder fractional engine showed that after breaking in on oil with a neutralizing additive the coefficients of friction did not descend to values which were observed after breaking in on oil with detergent additive. The authors drew this conclusion: on oils with high-alkali neutralizing additives, in contrast to detergent additives, the running in of piston rings was not finished.

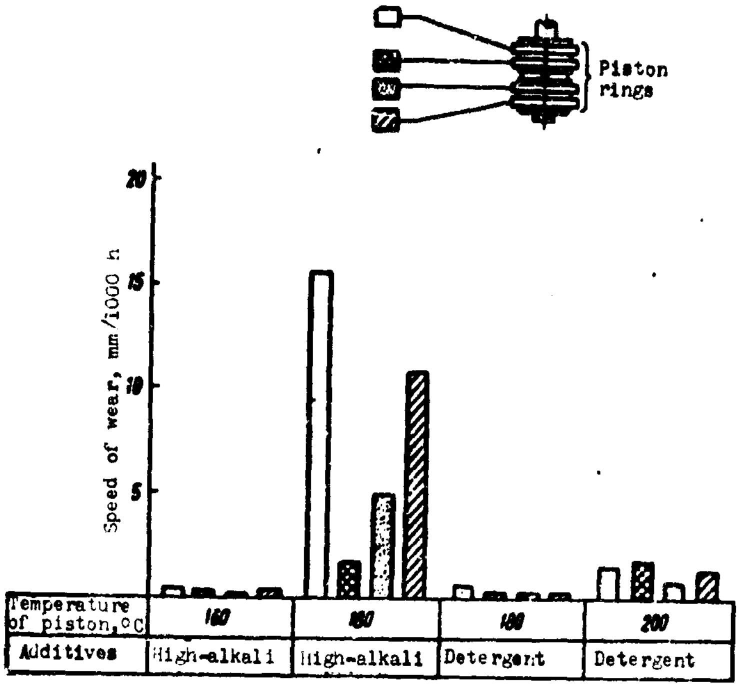

Fig. 97. Influence of temperature of a piston on the speed of wear of piston rings during tests of oils with high-alkali neutralizing and detergent additives on a one-cylinder engine. The diagram on the figure shows the wear of which rings are given in the diagram.

Table 30 gives data on the alkalinity and ash content of tested oils with neutralizing and detergent additives. One can see a great distinction in the properties of the oils.

Wakuri and coauthors [30] assumed that the distinction in properties of oils with examined additives affects the wear of piston rings during increased operating temperatures, since there occurs different wetting by oils with these additives of the heated surface of the metal. Wetting was studied by means of determination of spreading of the film of oil by a steel plate heated to 250°C with the applying of a drop (0.01 mℓ) of oil on its surface. It turned out that oils with high-alkali neutralizing additives possess considerably lesser wetting than oils with detergent additives (Fig. 98 reflects results of investigations of oils whose properties are given in Table 30).

Table 30. Alkalinity and ash content of oils with neutralizing and detergent additives for ship engines.

Property of oils	Oil with neutralizing additives				Oil with detergent additives			
	G	H	I	J	K	L	M	N
Alkalinity, mg KOH/g	34	34	34.3	32.7	0.50	2.40	3.29	7.55
Ash content, %	4.66	4.68	4.27	4.50	0.62	0.60	0.52	0.19

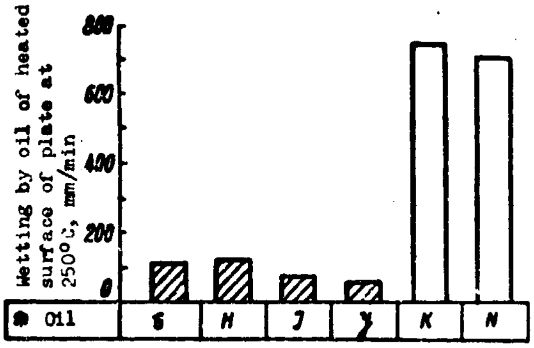

Fig. 98. Influence of high-alkali neutralizing and detergent additives on wetting by oil of the surface of a steel plate heated to 250°C: ■ — oil with high-alkali additive; □ — oil with detergent additive.

Thermal stability of these oils was also investigated and it was established that, as a rule, oils with neutralizing high-alkali additives (especially calcium) possess insufficiently high thermal stability and therefore at high operating temperatures will form many deposits, which hinder the creation of a normal lubricating film on the rubbing surfaces.

In the opinion of authors of these investigations, lesser wetting and lower thermal stability lead to the fact that under conditions of the worst supply of oil on the surface of the cylinder at lower and upper dead points of the stroke there occur seizings on separate sections of the surface of the piston rings and, accordingly, increased wear of the rings.

In our investigations there is also noted increased wear of radioactive piston rings of a four-cylinder carburetor engine [GAZ-51 [265]] (ГАЗ-51 [265]) and one-cylinder diesel engine 1-Ч-85/11 during operation of them on oil with the high-alkali additive [PMSYa] (ПМСЯ) under conditions of high-temperature and on low-sulfurous fuel. Such increased wear of the piston rings occurred in spite of the fact that this additive provides sufficiently effective protection from corrosional and electroerosional wear and also effectively protects antifriction bearing alloys from corrosion, as was shown above. The additive PMSYa also possesses a very effective stabilizing action (which is frequently called a dispersive), owing to which, obviously, it provides high purity to parts of the engine.

In particular, this was established with the help of the radioisotope method of lacquer deposition in engines developed by us jointly with P. F. Yurchenko and V. Ya. Nizhnik [80, 269]. The method is based on measurement of the quantity of lacquer film by absorption in it of β-radiation Co^{60}. This radioactive isotope has a long half-life (5.3 years), which is especially important for carrying out long-term bench and performance tests of the oil products. At the same time it possesses low energy of β-radiation (0.31 MeV), which permits measuring extremely thin layers of deposits (less 1 μm).

For activation on the lateral surface of the piston there are selected sections characteristic from the point of view of lacquer formation not subject to abrasion. The configuration and dimensions of them can be very diverse and are dependent upon construction of the piston. They are activated by applying on selected sections of the surface of the piston a solution $Co^{60}(NO_3)_2$, and then they are subjected to thermal diffusion annealing a muffle furnace. To prevent accidental penetration of the radioactive substance into the system of lubrication of the engine activated sections of the piston can be covered by a thin (not more than 5 μm) protective layer of chromium, nickel or other material.

The quantity of lacquer on the piston after a test of an oil or oil with an additive is determined with the help of an end-window

Geiger counter. The Piston is placed, as one can see from Fig. 99, into the measuring chamber with a holding device, allowing to establish before the small window of end-window counter alternately different activated sections.

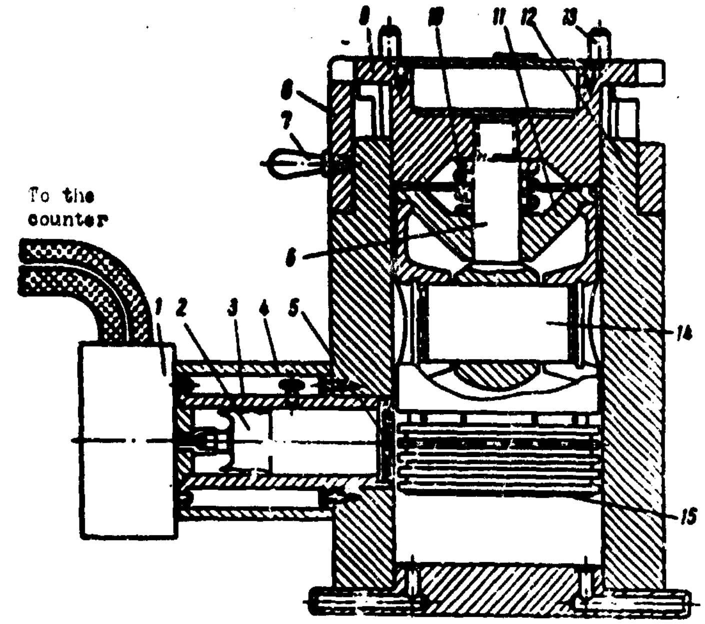

Fig. 99. Diagram of measuring chamber for determination of radioactivity on activated sections of the piston: 1 - input unit of the radiometric apparatus; 2 - end-window Geiger counter of the T-25 BFL type; 3 - housing of the counter; 4 - shield of counter; 5 - diaphragm; 6 - journal; 7 - handle; 8 - adjusting ring; 9 - holder; 10 - spring; 11 - support disk; 12 - housing of chamber; 13 - guide pins; 14 - piston finger; 15 - piston.

In the holding device the piston 15, with the help of the piston finger 14, is connected with journal 6 rigidly fastened in the holder 9. To eliminate movement about the axis of the piston finger the piston is held by a spring 10 acting on the support disk 11. Thus the secured piston is set in the housing 12 of the chamber. The vertical position of piston in the chamber is fixed by guide pins 13 evenly located along the circumference of housing 12. Horizonal setting of the piston in the assigned level with respect to the axis of the counter 2 is carried out with the help of an adjusting step ring 8 whose position is changed by turning the handle 7. The number of steps of the ring corresponds to the number of zones of radiation (activated sections) located on generatrixes of the piston. Connected to the end-window counter 2 of the [T-25 BFL] (T-25 БФЛ) type, installed in the steel housing 3 is an input unit 1 of the radiometric apparatus. To decrease the background noise the housing of the counter was protected by a lead shield 4. Put before the window of the counter is a diaphragm 5, which delays penetration into the counter of β-radiation from adjacent activated sections. The diameter of the diaphragm hole was selected depending upon the distance between the activated sections within 3-10 mm. The distance from the piston to the counter is 2 mm.

An estimate of the quantity of lacquer film, formed on the surface of the piston during the time of the test of the oil product in the engine, is produced by the change in intensity of radiation of activated sections of the piston. For this the intensity of radiation of every activated section of the piston before and after the test of the oil product in the engine was measured.

With the help of standardization a calibration graph is constructed which allows expressing the quantity of lacquer in milligrams per square decimeter. A change in intensity of radiation by 1% corresponded to the formation of lacquer film in a quantity of 10 mg/dm^2. Divergence between parallel determinations of lacquer deposition during the selected duration of measurement of radioactivity (4 min) did not exceed 1.0 mg/dm^2.

Figure 100 gives results of the estimation of lacquer deposition ability of motor oils and oils with additives on different (in temperature) sections of the piston. Tests of oils were conducted on engines [IT 9-2] (ИТ 9-2) [270]. As can be seen from Fig. 100, the method provides a differentiation estimate of lacquer depositing ability of oils both with and without additives. From Fig. 100 one can see the effective reduction of the quantity of lacquer on the piston during operation of the engine on oil with the additive PMSYa.

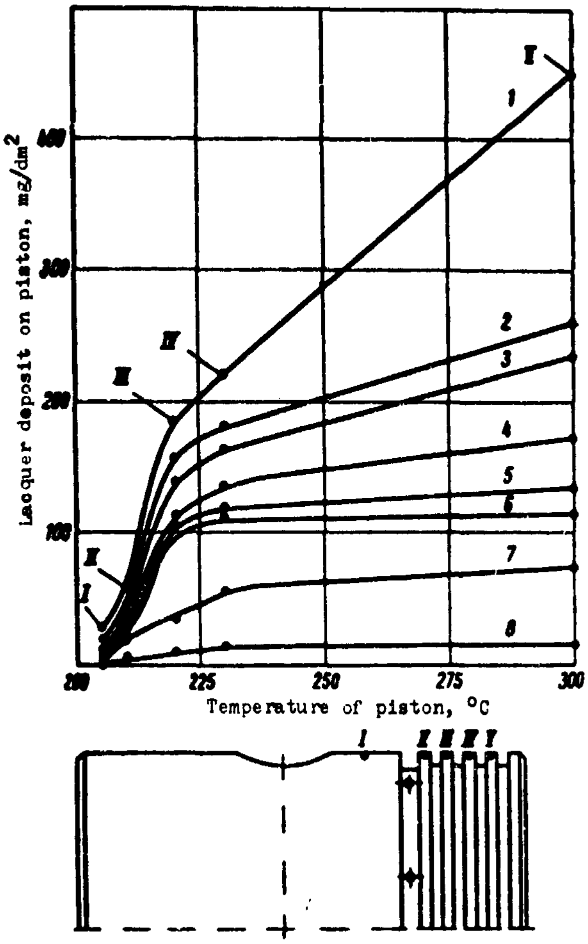

Fig. 100. Results of the determination of lacquer deposition ability of different oils and oils with additives by the radioisotope method on the engine IT 9-2: 1 – [AS-5 NKZ] (АС-5 НКЗ) (NKZ – Novokuybyshev works); 2 – [MS-20] (МС-20) Groznyy; 3 – AS-9.5 NKZ; 4 – [MK-22] (МК-22); 5 – AS-9.5 NKZ + 3% [TsIATIM-339] (ЦИАТИМ-339); 6 – AS-9.5 NKZ + 5% [VNII NP-360] (ВНИИ НП-360); 7 – AS-9.5 NKZ + + 4.5% [IP-22K] (ИП-22К); 8 – AS-9.5 NKZ + 5.5% PMSYa.

In recent years many researchers have begun studying the influence of high-alkali and other additives providing cleanness of parts of an engine on the wear of piston rings, including by means of radioisotope methods of investigation [265, 271, 272].

Proceeding from the assumption that the basic factor affecting the increase in wear at high operating temperatures is the process of oxidation of the oil, we developed a laboratory radioisotope method of simultaneous investigation of counterwear and detergent properties of motor oils under conditions of oxidation [265]. Figure 101 shows a diagram of one of the variants of the laboratory experimental apparatus.

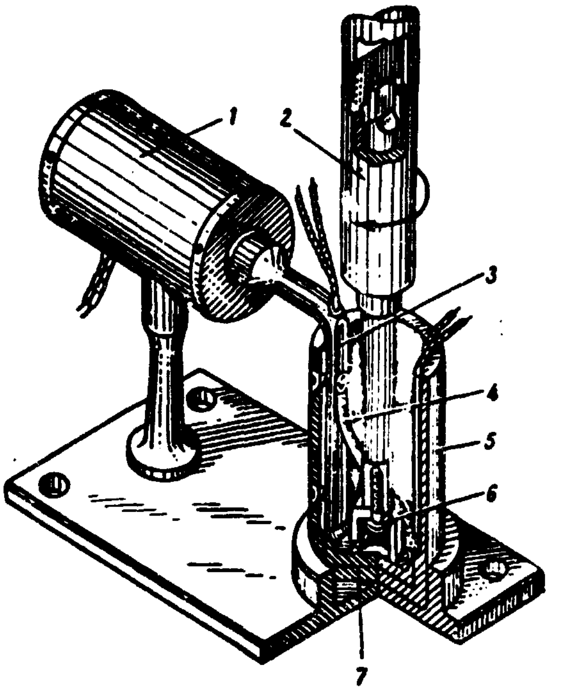

Fig. 101. Diagram of laboratory experimental apparatus for simultaneous investigation of counterwear and lacquer depositing properties of motor oils and oils with additives under conditions of oxidation: 1 – electrical heater; 2 – spindle; 3 – lacquer depositer; 4 – oil sprayer; 5 – bath 6 – radioactive sample; 7 – bottom.

The apparatus constituted a bath 5 made of teflon with a pressed cast iron bottom 7, about which a hollow cylindrical cast iron sample 6 slips at a speed of 730 r/min under a load of 10 kg/cm^2. The sample 6 was activated by insertions of Co^{60}. Mounted into the wall of the bath 5 was an aluminum segment, into which was inserted a steel lacquer depositer of Γ-shaped form 3. The edge of the flat working surface of the lacquer depositer 3 did not advance beyond the internal cylindrical surface of the teflon bath. With the help of the electric heater 1 the temperature of the lacquer depositer 3 during the carrying out of tests was maintained at a level of 250°C.

Table 31. Results of radioisotope simultaneous investigation of counterwear and detergent properties of motor oils under conditions of oxidation.

Tested oil	Wear, imp/min	Index of correct detergent effectiveness	Quantity of lacquer, mg/cm^2
Oil DS-14 without additive	11,800	0.23	1.36
The same oil + 15% VNII NP-370 + 6% PMSYa	22,200	0.005	0.27

[DS-14 = DC-14]

Filled into the bath 5 were 25 cm^3 of tested oil, sprayed with rotation of the spindle 2 by a spiral tubular sprayer 4 fastened to it. In the process of the test the oil was heated approximately to 190°C from the lacquer deposit and rubbing surfaces. The duration of each test was 5 hours.

Wear during the time of the test was determined by measuring the radioactivity of the bath with the oil before and after the experiment. The quantity of lacquer deposited during the time of the test was determined by measurement of the absorption of β-radiation of radioactive mark inscribed on the working surface of the lacquer depositer [269]. Furthermore, according to the radiation of the products of wear their quantity on the surface of the lacquer depositer was determined. The ratio of the quantity of radioactive products of wear of the surface of the lacquer depositer to the magnitude of wear was taken as the index of correct detergent effectiveness. Table 31 gives results of the test of a motor oil from sulfurous oils and the same oil with a composition of alkali additives. From the table it is clear that with the help of the developed method of simultaneous investigation of wear and lacquer deposition, under conditions of oil oxidation, it is possible to attain a differentiated estimate of properties of additives.

CHAPTER 7

INVESTIGATION OF THE INFLUENCE OF DIFFERENT ADDITIVES ON COUNTERWEAR PROPERTIES OF LIQUIDS FOR HYDRAULIC SYSTEMS

In recent years there have been published results of researches on the application of radioisotope methods for the study and appraisal of properties of liquids for hydraulic systems.

Weaver [273] developed the method of accelerated separation tests of liquids for hydraulic systems founded on the use of a pump unit of a hydraulic system with parts irradiated by neutrons in a nuclear reactor. Pump is installed on a specially designed stand whose diagram is shown in Fig. 102. In the creation of this stand it was considered that the minimum settling out of products of wear from the tested liquid circulating about the system will be attained with small dimensions of particles of products of wear and high purity of surfaces of parts and pipelines.

As can be seen from Fig. 102, installed into the system of the tested stand of stand at the outlet of the pressure section of the pump is a filter with holes of 2 μm, which limits the maximum dimensions of the particles of products of wear circulating about the system together with the tested liquid. Parts of the system and pipelines are made of polished stainless steel.

The blade pump provides circulation of tested liquid about the system with a total capacity of 9.45 ℓ with efficiency of 19 ℓ/min at 1200 r/min and pressure of 700 kg/cm^2. As can be seen from Fig. 102,

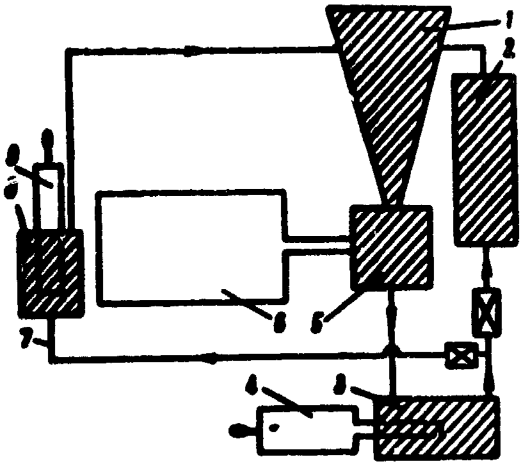

Fig. 102. Diagram of a stand for radioisotope accelerated tests of liquids for hydraulic systems: 1 – tank; 2 – oil radiator; 3 – filter; 4 – scintillation counter; 5 – pump; 6 – electric motor; 7 – polyethylene pipeline; 8 – measuring chamber; 9 – scintillation counter.

all tested liquid circulating about the system under high-pressure is pumped through the filter, and further a small part of the liquid under a pressure of 7 kg/cm^2 passes through a bypass into the measuring chamber and tank. The basic part of the tested liquid passes after the filter through the throttling valve, enters into the oil radiator, is cooled, and then passes into the tank from which by gravity flow proceeds again into the pump.

Radioactivity is measured by two scintillation counters, set, as one can see from Fig. 102, in the filter and measuring chamber. In the filter radiation of big particles of products of wear delayed by the filter is recorded and in the measuring chamber – radiation of particles circulating together with the tested liquid.

A test is conducted for 6 hours at a temperature of liquid in the system of 65°C. Before every test there is made a "calibration" test for standard liquid in standard conditions: 1 h heating, 6 h wear tests and about 1 h double washing of the system by the liquid which will be tested. During heating pressure developed by the pump is increased every other 10 min by 140 kg/cm^2.

Wear of the radioactive part after the test is determined by the formula

$$\Delta G = N_1\Delta R_1 + N_2(\Delta R_2 - k\Delta R_1),$$

where ΔG is the wear in mg; N – coefficient of standardization, mg/(imp/min); k – constant of recording equipment; ΔR – change in radioactivity, imp/min; $N_1 \Delta R_1$ – quantity of wornout particles circulating together with the liquid recounter with the help of standardization, mg; $N_2(\Delta R_2 - k\Delta R_1)$ – quantity of wornout particles delayed by filter recounted with help of standardization, mg.

Table 32. Comparison of results of radiometric determinations with results of weighting during a test of liquid for hydraulic systems.

Duration of test, h	Total loss of weight of ring, mg		Duration of tests, h	Total loss of weight of ring, mg	
	according to data of radiometric determinations	according to data of weighting		according to data of radiometric determinations	according to data of weighting
36	13.82	14.8	135	67.04	69.3
96	45.44	46.2	175	73.25	73.8

On the stand created Weaver conducted special tests for checking the accuracy of radioactive tracer methods in comparison with the method of weighting. Placed in the pump was a radioactive ring, and every 20 hours the liquid in the system was changed in order to reproduce the influence of replacement of test liquids in the carrying out of comparative tests of many liquids. Periodically the ring was weighed, and data on the loss of weight was compared with results of radiometric determinations. From Table 32 one can see the good correspondence of results of determinations by both methods.

Results of six-hour tests of different liquids for hydraulic systems are given in Table 33 and 34 for showing the reproducibility of results obtained during radioactive tracer tests on the same pump and the recurrence of results during a test on different pumps.

It is established (see Table 35) that according to data of tests on a pump with a radioactive blade, other comparative results than on a pump with a radioactive ring are obtained. A radioactive ring

Table 33. Reproducibility of results radioactive tracer tests of liquid for hydraulic systems.

Number of test	Rate of wear of ring, µg/h	Number of test	Rate of wear of ring, µg/h
1	38	12	48
3	40	14	42
5	33		
7	42		Mean 40.5

Table 34. Recurrence of results of radioactive tracer tests of liquids for hydraulic systems.

Liquid	Rate of wear of ring, ug/h		Liquid	Rate of wear of ring, µg/h	
	first pump	second pump		first pump	second pump
B	5	9	D	90	70
C	33	44	E	709	338

Table 35. Results of comparative tests for pumps with a radioactive ring and radioactive blade.

Liquid	Rate of wear, µg/h		Liquid	Rate of wear, µg/h	
	blade	ring		blade	ring
F	16	47	H	63	26
G	51	39	I	137	60

was used on one pump and a radioactive blade on the other. Different results are explained by the unequal composition of metals of the ring and blade and, accordingly, by different speeds of the interaction of components of liquids with the blade and ring.

As can be seen from Table 36, results of comparative 6-hour radioactive tracer tests coincided well with data of long 1000-hour bench tests of the same liquids by the standard method.

Table 36. Comparison of comparative results of short-term radioactive tracer and 1000-hour tests (appraisal in points*).

Liquid	Radioactive tracer 6-hour test		1000-hour test	
	blade	ring	blade	ring
I	1	2	1	2
H	2	1	2	1
G	2	2	4	2
Y	3	2	2	2
E	4	3	4	3

---

*Best result - 1 point; worst result - 4 points.

Table 37 gives results of radioactive tracer tests on a pump with a radioactive blade with the selection of additives to liquids for hydraulic systems. From Table 37 it is clear that radioactive tracer tests provided very rapid detection of additives causing increased wear.

Table 37. Results of radioactive tracer tests of different additives to liquids for hydraulic systems.

Tested additive	Duration of test, h	Rate of wear, μg/h	Tested additive	Duration of test, h	Rate of wear, μg/h
W	< 1	>15,000	Y	< 1	>23,000
H	6	78	Z	6	91

An important peculiarity of these tests is the obligatory reduction in rubbing surfaces to the initial identical state by means of operation of the system on standard liquid without additives before the test of each additive. From Table 38 one can see how the speed of wear during operation of the system on a standard liquid was changed in each hour after a test of one of the additives (W). In these tests the initial speed of wear on the standard liquid was restored in 4 hours.

Table 38. Restoration of speed of wear during operation of the pump on standard liquid after test of an additive which caused high wear.

Period of test, h	Speed of wear of blade, μg/h	Period of test, h	Speed of wear of blade, μg/h
0-1	315	3-4	64
1-2	160	4-5	46
2-3	95	5-6	61

It is necessary to note the contradictory nature of data published in literature by different authors about the reduction of rubbing surfaces to the initial state after a test of additives (i.e., reduction to those dimensions of roughnesses which were noted before the test of additives). Thus, Jackson and Burk and coauthors [15] affirmed that the running in of rubbing surfaces of a one-cylinder engine with a radioactive piston ring after a test of additives effectively reducing wear was attained with standard oil without additives very quickly, whereas restoration of the initial speed of wear using standard oil after testing products causing increased wear required multiple repeated experiments on standard oil. This does not correspond to the aforementioned data of Weaver [30] and is directly opposite to results of investigations of Pouderoyan and coauthors [29], who established that during tests of oils with additives on diesel engines it was necessary to expend 50-100 h of work of the engine on standard oil without additive in order to wear out a modified layer of surface of metal (i.e., to wear out the film formed on rubbing surfaces by the additive) and to provide restoration of the initial speed of wear on the standard oil. We observed the same effect as that of Pouderoyan and coauthors during the above-stated investigations of oils under conditions of electroerosional wear.

The test of additives conducted by Weaver permitted establishing a very interesting effect: in the presence of detergent additives in liquid for hydraulic systems the dimensions of particles of products of wear were considerably lews than those in the absence of a detergent component and were not impeded by the filter circulating together with the liquid, as can be seen from Table 39.

Table 39. Influence of detergent additives on detention by filter of products of wear during radioactive tracer tests of liquids for hydraulic systems.

Test liquid	Recorded products of wear, %	
	in filter	in circulating liquid
With detergent additive 1	6	94
With detergent additive 2	14	86
Without detergent additive	100	0

Coleman [274] used the radioisotope separation method of tests of liquids for hydraulic systems with the selection of optimum composition of incombustible liquids, which are emulsion of water (40%) in mineral oil (60%) with emulsifying, antirust, counterseizing, and counterfoam additives and additives increasing the stability of the liquid. The method permits estimating the influence of additives on wear of radioactive parts (blades and rings) of a blade pump pumping liquid in a hydraulic system of a specially created stand in 3-4 h of tests of liquid instead of 400-1000 h of bench tests with the use of a pump with the standard parts.

The closed hydraulic system with a total capacity of 7.55 ℓ included a blade pump, throttling valve, cooling radiator, and measuring chamber. The pressure created by the pump was 700 kg/cm^2 and the temperature of the liquid, 65°C.

Radioactivity of the test liquid was recorded in the measuring chamber by a scintillation counter. An appraisal of results of the tests was produced by comparison of the speed of wear of the radioactive parts during operation on tested and standard liquids, and the comparative speed of wear was thus expressed.

Coleman especially notes that the application of such a radioisotope method provided a correct appraisal of counterwear properties of emulsion liquids with different additives for the short period of separation bench tests in contrast to the attempts to use for these purposes a test on the four-ball apparatus according

Table 40. Results of tests of emulsion liquids with additives on the stand (1000 hours) and on the four-ball apparatus.

Counterwear properties of tested liquid	Results 400-hour bench tests of wear: losses of weight of parts of the pump, %	Results of tests on four-ball apparatus: diameter of spot of wear, mm	
		inoperative liquid	liquid after 400-hour bench tests
Unsatisfactory	0.422	0.33	0.34
Satisfactory	0.061	0.31	0.30

to the frequently used method (1800 r/min; 7.5 kg; 1 h). As can be seen from Table 40, liquids which have undergone with positive and negative results prolonged 400-hour bench tests on the four-ball apparatus were not differentiated.

The correctness of the appraisal of counterwear properties of emulsion liquids with the help of short-term radio isotope tests is established in the comparison with results of standard 400-hour bench tests (Fig. 103). One can see the good correspondence of comparative results of tests by both methods.

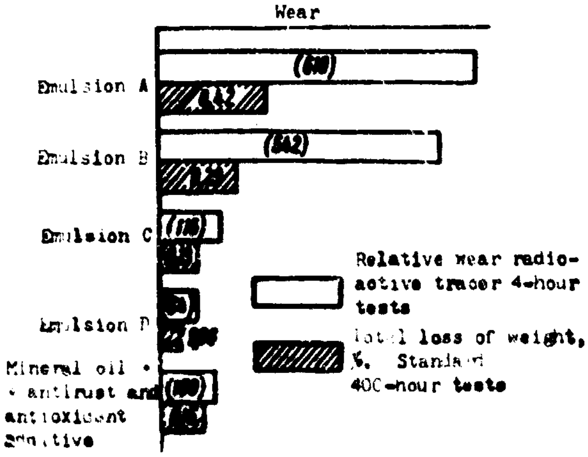

Fig. 103. Comparison of results of short-term radioisotope and prolonged 400-hour bench tests of emulsion liquids for hydraulic systems.

Figure 104 gives results of separation radioisotope tests in the search of an optimum composition of emulsion liquid with a composition of counterwear, antirust, and emulsifying additives.

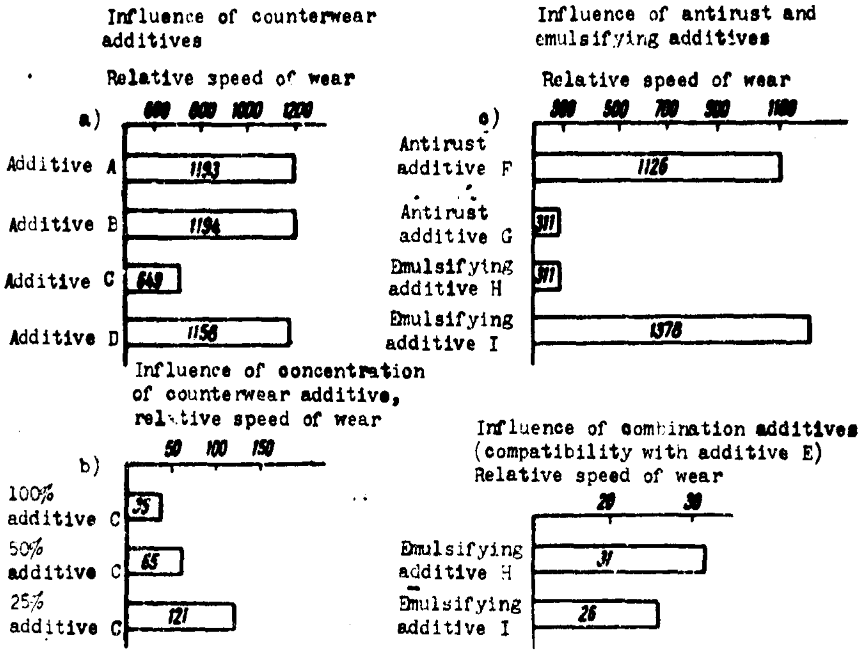

Fig. 104. Results of separation of radioisotope tests of additives to emulsion liquids for hydraulic systems: a) selection counterwear additives; b) check of the influence of concentration of counterwear additive; c) selection of antirust and emulsifying additives; d) selection of combinations of additive E with emulsifying additives.

The considerable influence of certain additives on the speed of wear of radioactive parts of the pump is revealed. Thus a change in antirust component, in spite of its small concentration (less 0.5%), as one can see from Fig. 104c, caused a sharp change in the speed of wear. Emulsifying additives very intensively affected the speed of wear, as can be seen from Fig. 104c. Thus, additive I, which provided the obtaining of very stable emulsions, caused a very sharp increase in the speed of wear. However in combination with additive E, as can be seen from Fig. 104d, both emulsifying additives H and I did not cause intense wear.

On the basis of his great experimental work, Coleman [274] arrives at the conclusion that with the development of an optimum composition of incombustible emulsion liquids for hydraulic systems correctly balanced combination of additives of different functional assignment are very important. Such a combination should provide along with other properties minimum wear of parts of the pump. The selection of such a combination is considerably accelerated and is facilitated with application of the radioisotope method of short-term separation tests.

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U. S. BOARD ON GEOGRAPHIC NAMES TRANSLITERATION SYSTEM

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

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