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Technical Operation and Service of Cars Department named after  
Govorushchenko M. Ya.

Nahluk M.

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The abstract outlines the basics of the technology for the production of operating materials, the requirements for them, the main properties and methods of testing materials. The main varieties, types and brands of fuels, operating materials and technical fluids used in the operation and maintenance of vehicles are given.

Intended for bachelors of all forms of study according to the educational program «Motor vehicle transport».

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# LECTURE 1. GENERAL INFORMATION ABOUT OIL AND ITS PROCESSING TECHNOLOGY

Lecture plan:

1.1 Introduction.

1.2 Origin of oil and its production.

1.3 The chemical structure of oil, its influence on the properties of fuel and lubricants.

1.4 Fractional, group and elemental composition of oil and its processing products.

1.5 Obtaining fuel and lubricants from oil.

1.6 Cleaning of fuels and oils.

1.7 Control questions.

## 1.1 INTRODUCTION

A unique system has been formed and operates in the world, which includes man, the technosphere, and the biosphere. The technosphere refers to all technical means created by man, and the biosphere refers to the surrounding living nature. The core of the technosphere is the machine-energy complex. In this complex, the engine as a converter of fuel energy into mechanical energy plays an important, if not the leading, role. Since one of the main conditions for the normal and efficient operation of the engine is the quality and correct use of fuels, lubricants and coolants, they become the most important connecting link of the entire biotechnical system.

**Hematology** – is a young science, it is just beginning to develop, but since certain issues are considered from a hematological point of view, it is useful for a specialist in the field of engine construction to familiarize himself with the general, principled provisions of this science.

Hematology as a science developed at the junction of chemistry and motor engineering. A modern specialist in the field of engine construction must be familiar with the basics of hematology. The optimal design decisions that should be made during the creation of any internal combustion engine can be found and implemented only by taking into account the properties and capabilities of fuels and lubricants.

Nowadays, the need for a systematic approach to the comprehensive development of both the motor industry and the oil refining industry has become obvious. When ensuring the optimal performance **of the engine – fuel – lubricants – cooling liquids**, it becomes possible to obtain the highest efficiency of use of all components of this system.

At the current scale of internal combustion engines, a change of even a fraction of the percentage of use of the energy potential of fuels leads to saving or overspending of millions of tons of fuel. Improper use of lubricants, inconsistency of the quality indicators of motor oils in the design of the engine can lead not only to excessive consumption of fuel and lubricants, but also to a significant reduction in the reliability of the engine, and an increase in its harmful effect on the biosphere.

The annual consumption of fuel and lubricants worldwide has now reached several hundred million tons. Despite the significant increase in the fuel efficiency of engines, the consumption of fuel and lubricants continues to grow due to the increase in the number of

engines. The total capacity of automobile engines alone is currently more than 30 billion kW, and gasoline consumption is more than 400 million tons per year.

In recent years, the automotive industry has implemented a large program of dieselization of cars, which will save millions of tons of fuel (not including the conversion of some trucks to natural and oil gas). The use of electronics, including the use of microprocessor technology in engine and transmission control, makes it possible to increase the fuel efficiency of gasoline engines by 10-15%.

A very important prerequisite for the study of hematology is also the significant impact of quality indicators of fuels and lubricants on the environment. Targeted management of the ecological system is impossible without knowledge of hematology. For example, a certain relationship between the toxicity of engine exhaust gases and the fractional and group chemical composition of the fuel, the presence of sulfur in it, etc. has been established.

## **1.2 ORIGIN OF OIL AND ITS PRODUCTION**

Oil was and remains the main raw material for obtaining modern fuels and lubricants for internal combustion engines.

There are three hypotheses for the origin of oil.

**1st hypothesis.** The most modern and widespread is the hypothesis of organic (biogenic) origin, according to which oil was formed from the remains of plants and animals accumulated in the sedimentary rocks of the seas and oceans. Having found themselves in the bowels of the earth, they underwent complex chemical changes for millions of years under conditions of high temperatures and pressures in the presence of various natural catalysts. As a result, primary oil deposits were formed in the deep regions of the earth's crust.

From primary deposits, oil gradually moved (migrated) through cracks, sandy and porous rocks and accumulated at various depths in voids of the earth's crust, forming secondary deposits, i.e. filling zone, from where it is currently mined.

**2nd hypothesis.** There are supporters of the hypothesis of an inorganic (abiogenic) origin of oil. For the first time, it was most fully expressed by D.I. Mendeleev, who believed that oil was formed from metal carbides and water vapor under the conditions of deep processes occurring in the earth's crust under the influence of high pressures and temperatures.

**3rd hypothesis.** There are supporters of a comprehensive approach to the issue of the origin of oil. They believe that there could have been both mechanisms of oil formation (organic and inorganic), which complemented each other to a certain extent or acted at different stages of the process.

Let's consider the biogenic hypothesis in more detail. The main argument of its supporters is the territorial coincidence of oil fields and zones of sedimentary rocks. For example, a large number of oil deposits in the zone of the shelf of seas and oceans, coastal zones, zones where there was a seabed in remote geological periods, etc.

However, in recent years, large accumulations of oil associated with sedimentary rocks have been discovered. This made it possible to assume, as a variant of the biogenic hypothesis, that the processes of oil formation from organic material that got into the deep bowels of the earth are possible not through gradual sedimentation, but as a result of

geological processes characteristic of the early periods of the formation of the earth's surface

According to the classical biogenic hypothesis, the initial stage of the process of oil formation was the decomposition of animal and plant remains under the influence of atmospheric oxygen and bacteria with the formation of gases and other products.

Gases (mainly  $\text{CO}_2$ ,  $\text{N}_2$ ,  $\text{CH}_4$ ,  $\text{NH}_3$ ) dispersed in the atmosphere, dissolved in water and were absorbed by natural adsorbents.

Part of the original organic material, the most resistant to oxidative processes and bacterial influence, remained in sedimentary rocks and gradually sank into their thickness or, as a result of tectonic processes, ended up in the deep bowels of the earth several kilometers from the surface, having entered a reducing environment under a pressure of up to 30 MPa at a temperature of 150...250°C, and the presence of natural catalysts, these products (consisting mainly of fats) for many millions of years turned into oil - a complex mixture of various hydrocarbons and other organic compounds.

The first well in the world was drilled in 1848 by F.A. Semenov is a small-scale fishing technician near Baku.

After the appearance of internal combustion engines, and later the car, the development of oil production became larger and larger every year.

By the mid-1970s, the world's explored oil reserves amounted to 82 billion tons. The unique properties of oil and the fuels obtained from it led to its leading role as an energy carrier. But in connection with the huge consumption of oil and the complication of its production, there was a need to solve the issues of gradual transition to new forms of energy technology, the basis of which is nuclear, and later thermonuclear energy. In addition, every year it becomes more and more clear that the unique properties of oil fuels are difficult to implement on the basis of substitutes for gasoline and diesel fuel. Therefore, more and more coal deposits will be developed with further processing of coal into synthetic liquid fuel.

Hydrogen obtained from water through the use of thermonuclear and solar energy will probably find wide application as a fuel.

### **1.3 CHEMICAL STRUCTURE OF OIL, ITS INFLUENCE ON THE PROPERTIES OF FUEL AND LUBRICANTS**

The bulk of the oil substance consists of carbons of three main groups: paraffinic (alkanes), naphthenic (cyclans) and aromatic (arenes), the composition and properties of which depend on the origin and place of oil extraction. The structure of oil is presented in figure 1.1.

Paraffin hydrocarbons have a high freezing point, which makes their presence in winter fuels and lubricants undesirable.

The total content of paraffinic hydrocarbons in oil and refined products is about 50-60%, and their content is highest in fractions boiling up to 150°C.

Naphthenic hydrocarbons with the same molecular weight as paraffin are more inert to oxidation at low temperatures. Naphthenic hydrocarbons have a low melting point, so they lower the freezing point of oil products, which is a valuable component of winter fuels and lubricants. Due to the resistance of naphthenic hydrocarbons to oxidation at high temperatures, gasoline has good anti-knock properties.

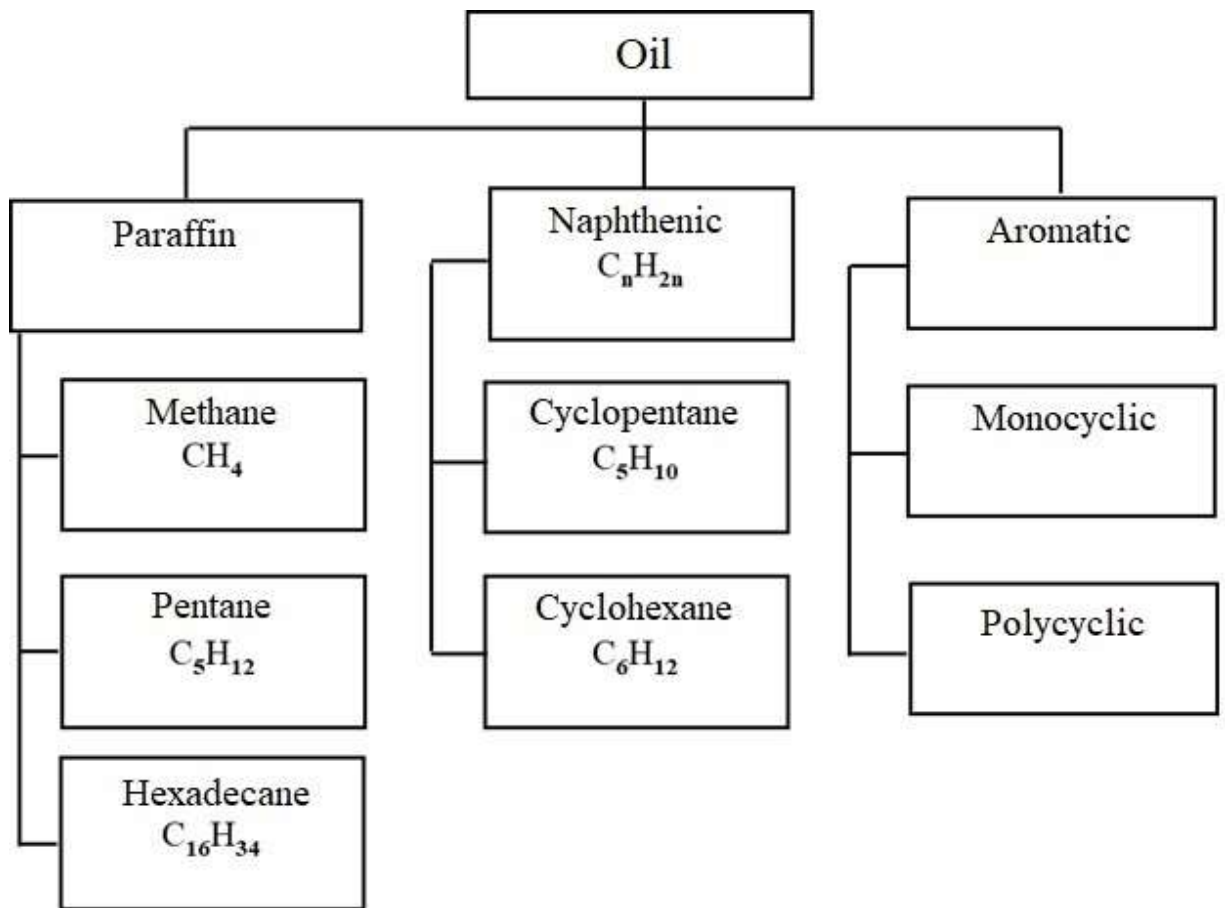


Figure 1.1 – General structure of oil

The content of naphthenic hydrocarbons in oil ranges from 20 to 30%, and in oil fractions it reaches 70%.

Aromatic hydrocarbons have high thermal resistance to oxidation reactions. These hydrocarbons are characterized by high values of viscosity, density, and boiling point. When the temperature decreases, the viscosity of the arenas increases sharply, which affects the properties of lubricants.

The presence of aromatic hydrocarbons in gasoline improves their anti-knock properties, and in diesel fuels, it worsens self-ignition and makes diesel work harder.

Oils contain from 10 to 48% aromatic hydrocarbons.

In addition to hydrocarbons of the three main groups, oil contains unlimited hydrocarbons, organic acids, tar-asphalt substances, mineral impurities, sulfurous and nitrogenous compounds.

Unsaturated hydrocarbons are formed in the process of thermal processing of oil. They are easily oxidized and prone to joining and densification reactions. Due to the low stability of unsaturated hydrocarbons, their presence in fuel and lubricants is undesirable.

Organic acids are compounds containing oxygen. The main organic acids in oils are naphthenic. They actively interact with non-ferrous metals, forming salts. A large amount of naphthenic acids is contained in fuel-gasoil fractions of oil.

Tar-asphalt substances are complex compounds of carbon, hydrogen, oxygen, sometimes sulfur, which partially replaces hydrogen. Resin-asphalt substances are divided into neutral oil resins, asphaltenes, carbenes, and acidic oil resins. Tar-asphalt substances

are insoluble and deteriorate the quality of oil products, so their presence in light fuels is unacceptable.

Sulfuric compounds are divided into active ones that directly react with metals (hydrogen sulfide  $H_2S$ , elemental sulfur  $S$ , mercaptans) and inactive (neutral) compounds that do not affect metals.

Neutral compounds make up the bulk of sulfur compounds - 70...80%. The presence of active sulfur compounds in oil products is not allowed.

Nitrogenous compounds are contained in oils in small quantities (0.03...3%) and are practically removed during the refining of oil products.

## 1.4 FRACTIONAL, GROUP AND ELEMENTAL COMPOSITION OF OIL AND ITS PROCESSING PRODUCTS

Oil is a viscous, oily liquid with a characteristic smell. Its color depends on the resins dissolved in it: dark brown, brown-green, and sometimes light, almost colorless. Oil fluoresces slightly in the light. It is lighter than water and always forms spreading spots on the water surface (up to a monomolecular layer). The density of oil depends on the deposits and ranges **from 770 to 880 kg/m<sup>3</sup>**.

The kinematic viscosity of most oils rarely exceeds 40...60 mm<sup>2</sup>/s at 20°C. Oil does not dissolve in water, but with intensive mixing it forms stable emulsions that slowly separate. Since oil is a complex mixture of individual hydrocarbons, it does not have certain physical constants, such as boiling point, freezing point, etc.

When considering the physical and chemical properties of oil, three types of its compositions are distinguished: **fractional, group chemical and elemental**.

**Fractional composition of oil.** At atmospheric pressure and an increase in temperature, different individual hydrocarbons are successively evaporated from oil. Depending on the temperature range in which oil products boil, they are grouped into different fractions. Therefore, a group of hydrocarbons that boils in a certain temperature range is called a fraction.

Below are the temperature ranges (°C) at which generally accepted fractions of oil boil off.

Gasoline.....	35 – 205
Fuel for jet engine.....	120 – 315
Diesel fuel.....	180 – 360
Gasoil.....	230 – 360

After distilling off these fractions, a dark viscous liquid remains, called heating oil. For a long time, until the end of the 19th century, heating oil was not used in industry, it was a waste product of oil refining. This was explained by the fact that its further processing was associated with great difficulties, since the temperature of distillation of heating oil fractions at atmospheric pressure is higher than the temperature of their thermal destruction, that is, the breaking of molecules into parts under the influence of temperature. It was possible to separate heating oil into fractions only under reduced pressure (4...6 kPa). This process, called vacuum, made it possible to obtain solar fractions and distillate lubricants (light, medium and heavy) from heating oil, including base oils for internal combustion engines.

After distillation of oil fractions from heating oil, tar or semi-tar remains, which are used to obtain residual oils and bitumen.

**Group chemical composition of oil and products of its processing.** The group chemical composition of oil is the content of hydrocarbons of certain chemical groups, which are characterized by the ratio and structure of the compound of carbon and hydrogen atoms.

Chemical groups (homological series) of hydrocarbons are characterized primarily by the quantitative ratio of carbon and hydrogen atoms. This relationship is expressed by the general formula of the group.

Let's consider the main ones; groups of hydrocarbons contained in oil and products of its processing.

**Alkanes** (paraffin hydrocarbons) are saturated hydrocarbons (they have no double bonds). The general chemical formula of alkanes  $C_nH_{2n+2}$  (where “n” – is the number of carbon atoms).

The amount of alkanes in oils depends on the oil field and is 25-30%. In the oils of some fields, taking into account the gases dissolved in them, the content of alkanes reaches 50...70%. In different fractions of the same oil, the content of alkanes is usually different and decreases as the molecular weight of the fraction and its boiling point temperature increase. For example, in the main fraction of oil boiling up to 300°C, the content of alkanes reaches 88%. In the residual fractions, their content decreases to 5...10%.

According to their structure, alkanes are *normal and isoalkanes*.

The structure of normal alkanes is an unbranched chain of carbon atoms, the free valences of which are occupied by hydrogen.

If a chain of carbon atoms has one or more branches, the structure is called isomeric, and alkanes having this structure are called *isoalkanes*.

The general formula is preserved ( $C_nH_{2n+2}$ ).

The isomeric structure of alkanes significantly affects their physical and chemical properties. The liquid boiling point and melting point of solid isoalkanes are generally lower than those of normal alkanes. Normal alkanes at low and moderate temperatures are usually very inert, including with respect to oxygen. This contributes, for example, to the high chemical stability of gasolines containing normal alkanes. Isoalkanes are less stable at moderate temperatures.

With increasing temperature, the stability of normal and isoalkanes gradually decreases, and the decrease in stability of normal alkanes initially occurs at approximately the same rate as that of isoalkanes, but at a temperature of 250...300°C, the rate of interaction with an oxidant in normal alkanes increases sharply and becomes significantly higher than in isoalkanes with the same molecular weight. Depending on the number of carbon atoms, alkanes have a gaseous, liquid or solid aggregate state. Alkanes, in which the number of carbon atoms “n” = 1...4, under normal conditions are gases (methane, ethane, propane, butane). When “n” = 5...15, these are liquids, and after n=16 (hexadecane), normal alkanes are solids (which are dissolved in oil and its processing products).

**Cyclanes** (naphthenic hydrocarbons) are also saturated hydrocarbons.

They have a cyclic structure, their general formula  $C_nH_{2n}$ . For the first time, cyclans were found in oil by the famous Russian chemists V.V. Markovnikov and V.M. Ogloblin. The content of cyclans in various oils ranges from 25 to 75%, and in certain fractions of some oils - up to 80%. Cyclans are contained in all oil fractions, and as the molecular weight and boiling point temperature of the fraction increase, their number increases.

Cyclanes can consist of monocyclic structures usually of five or six members (that is, CH<sub>2</sub> groups), as well as bicyclic, less often compounds of three rings. For polycyclic compounds, the general formulas have the form C<sub>n</sub>H<sub>2n-2</sub>; C<sub>n</sub>H<sub>2n-4</sub> and C<sub>n</sub>H<sub>2n-6</sub> depending on the number of cycles (i.e. rings). Cyclones consisting of three or four rings were not detected in the oils.

In terms of chemical properties and especially in terms of oxidative stability, cyclanes at normal temperatures are almost as stable as normal alkanes, and at high temperatures (400 °C and above) they approach isoalkanes in terms of stability, that is, they have greater chemical stability than normal alkanes

Some monocyclics and polycyclics have a hybrid structure in which chains of alkane structures are attached to the ring.

Oil refining products, especially thermal cracking gasoline, contain a significant amount of unsaturated hydrocarbons - *alkenes and alkadeins (olefins and deolefins)*.

**Alkenes** (their general chemical formula C<sub>n</sub>H<sub>2n</sub>) differ from alkanes by the presence of one double bond between carbon atoms. The double bond with its ability to break easily determines the low chemical stability of alkenes. They easily undergo an addition reaction, which is the reason for their rapid oxidation and oxidative polymerization. This explains the insufficient oxidative stability of thermal cracking gasolines, in which the content of unsaturated hydrocarbons reaches 40%.

Alkenes, as well as alkanes, have normal and isomeric structures, and isoalkenes are more diverse than isoalkanes, as they change their properties depending not only on the location and number of side chains, but also on the location of the double bond.

Alkadeynes have two double bonds, and this makes them even more unstable and reactive than alkenes. Their general formula is C<sub>n</sub>H<sub>2n-2</sub>.

The presence of alkadienes in oil products gives them a number of negative qualities, including a tendency to tar formation.

Alkenes and alkadeines are unsaturated hydrocarbons, and its presence in fuels is extremely undesirable, as it shortens their possible storage period. They are practically not contained in oils.

The simplest hydrocarbon of the aromatic series (arena) is benzene C<sub>6</sub>H<sub>6</sub>. It has a six-membered ring structure with three alternating double and single bonds.

For monocyclic arenes, the general formula has the form C<sub>n</sub>H<sub>2n-6</sub>.

The structure of more complex polycyclic arenes (for example, naphthalene) is based on the connection of two or more six-membered benzene rings.

The double bonds of arenes are stable and do not break even under the influence of nitric and sulfuric acids, when a substitution reaction of one of the hydrogen atoms (and not an addition reaction) occurs. The breaking of double bonds in arenes can be achieved only at high temperature and in the presence of catalysts.

The total content of arenes in oils is relatively small. In gasoline fractions, their content usually exceeds 5...25% and from an oil field. In heavier fractions, the content of arenes can reach 35%.

**Elemental composition of oil.** The elemental composition of oil is the content of individual chemical elements in it, expressed as a percentage by mass.

Analysis of oils from different fields showed that their elemental composition changes little. The main elements that make up oil and the products of its processing are carbon and

hydrogen. The average carbon content is 83.5...87%, and hydrogen is 11.5...14%. In addition to carbon and hydrogen, oil contains sulfur 0.01...5.8%, oxygen 0.1...1.3%, nitrogen 0.03...1.7% and traces of metals.

Carbon and hydrogen are part of oil in the form of various hydrocarbon compounds; oxygen and nitrogen are usually in a bound form (naphthenic acids, resins, phenols, amines, etc.). Sulfur can be both in a bound and in a free state.

Sulfur has a particularly negative effect on the operational properties of products obtained from oil, so its content is an important criterion for assessing the quality of oil.

Impurities contained in oils affect the quality of fuels and lubricants obtained from it. Modern methods of oil processing make it possible to completely free it from impurities and, first of all, from particularly harmful ones, such as sulfur and its compounds, oil resins and a number of others. However, it should be taken into account that the purification of oil or products derived from it is associated with significant costs of energy, reagents, time and labor, and some methods of purification - with the loss of a certain amount of valuable products and environmental pollution.

Sulfur in oils is found mainly in organic compounds and resins. The resins contained in oil are high-molecular compounds that, in addition to carbon, contain oxygen, sulfur, nitrogen, and metals. The content of resins in oil varies within the range (from 1 to 40% or more).

## 1.5 OBTAINING FUEL AND LUBRICANTS FROM OIL

The main method of oil processing is its direct distillation.

**Distillation – distillation (drip trickling)** – the separation of oil into fractions that differ in composition, based on the difference in the boiling points of its components.

**A fraction** – is a chemical component of oil with the same chemical or physical properties (boiling point, density, dimensions) that is separated during distillation.

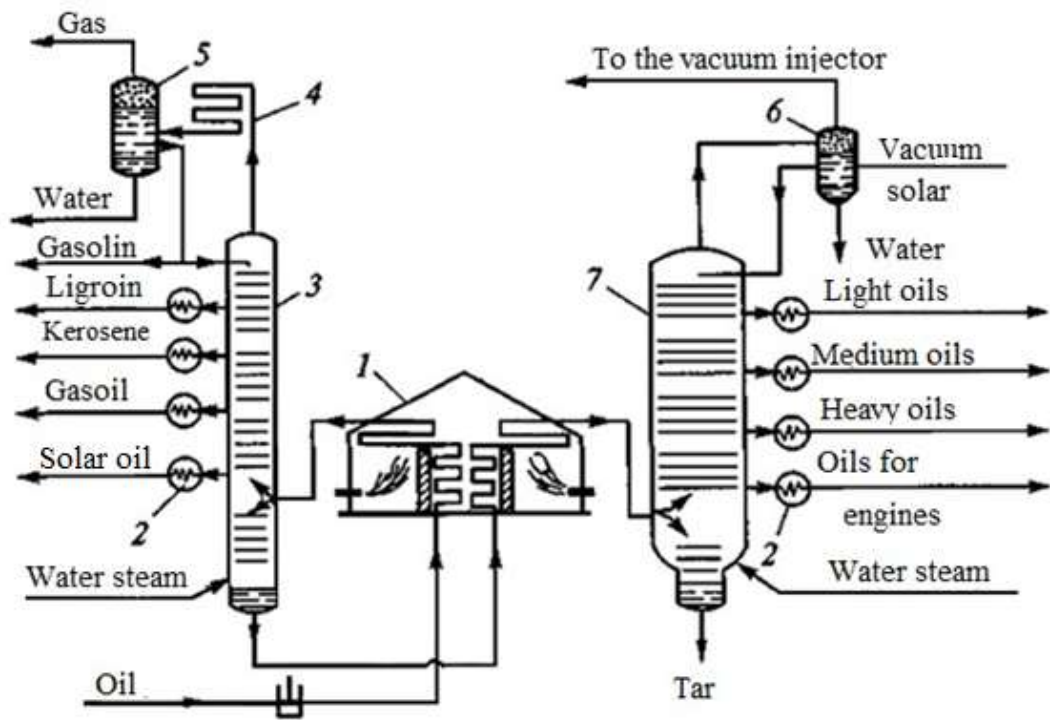
**Direct distillation** – is a physical method of oil processing using an atmospheric-vacuum installation (figure 1.2), the principle of which is as follows.

As a result of heating oil in a special tubular furnace 7 to 330...350°C, a mixture of oil vapors and liquid residue that has not evaporated is formed, which enters the rectification column 3 with heat exchangers 2.

In the rectification column (fig. 1.3), oil vapors are separated into fractions that make up different oil products. At the same time, the boiling point of adjacent groups of obtained fractions can differ by only 5 ... 8°C.

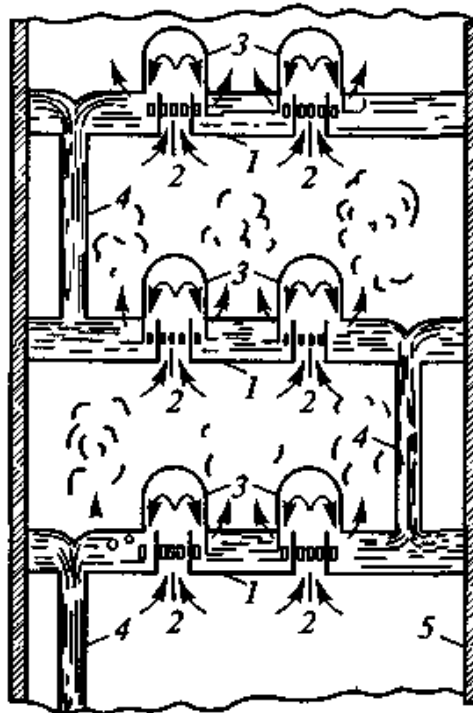
Heavy fractions of oil, entering the column in the liquid phase, are already separated from the vapors in its lower part and removed from it in the form of fuel oil.

Depending on the chemical composition of oil, two fuel production schemes are used (fig. 1.4). **In the first case**, in the range of boiling temperatures from 40 to 150°C, **aviation gasoline** is selected, and in the range from 150 to 300°C – **kerosene**, which is used to make jet fuels. **In the second case**, in the interval of boiling temperatures from 40 to 200°C, **automobile gasolines** are selected and in the interval from 200 to 350°C – **diesel fuels**.



1 – tubular furnace; 2 – heat exchangers; 3 – rectification column; 4 – capacitor;  
5 – separator; 6 – solar assembly; 7 – vacuum column.

Figure 1.2 – Schematic diagram of an atmospheric-vacuum installation for direct oil distillation



1 – metal plates; 2 – openings for the passage of steam; 3 – caps; 4 – drain pipes;  
5 – cylindrical body.

Figure 1.3 – Scheme of the cap column of the rectification

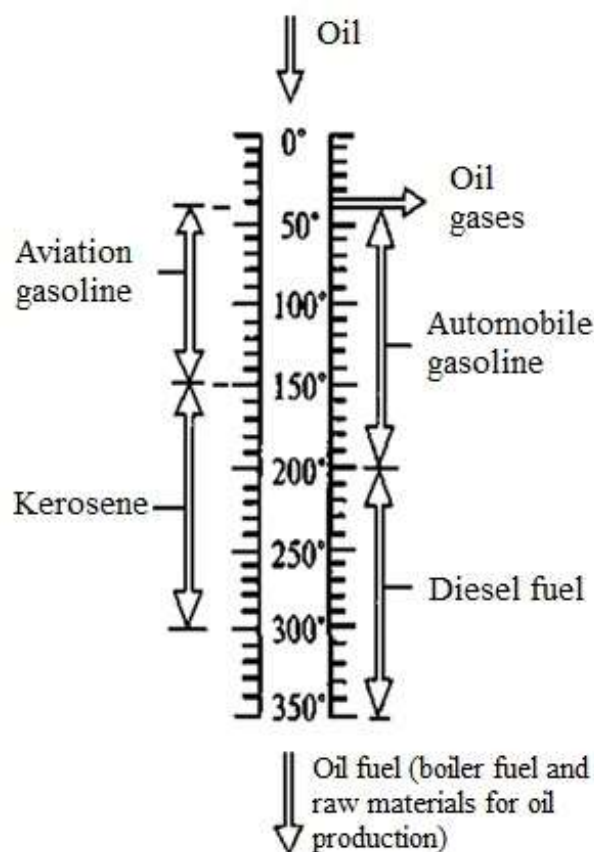


Figure 1.4 – Schematic diagrams of obtaining the most important types of fuel for engines during oil distillation

**The fuel oil** that remains after the distillation of fuel fractions (60...80% of the initial mass of oil) is used to obtain oils and cracked gasoline.

Hydrocarbons with a boiling point below 40°C (accompanying gases) are used as additives to some gasolines and as raw materials for obtaining a number of synthetic products, as well as as fuel for gas cylinder cars.

The products of direct oil distillation (see fig. 1.2) are the following distillates: **gasoline** (40...200°C); **ligroine** (110...230°C); **kerosene** (140... 300°C); **gas oil** (230...330°C) and **solar oil** (280...350°C).

The average yield of gasoline fractions, which depends on the properties of the extracted oil, ranges from 15 to 25%. Other fuels account for 20...30%.

**Ligroin**, which has a slightly higher density than gasoline (heavy gasoline), is used as diesel fuel and as a raw material for obtaining high-octane gasoline.

**Gas oil**, which is an intermediate product between kerosene and lubricating oils, is used as a fuel for diesel engines and is also a raw material for catalytic cracking.

Products obtained by the direct distillation method have high chemical stability because they do not contain unsaturated hydrocarbons.

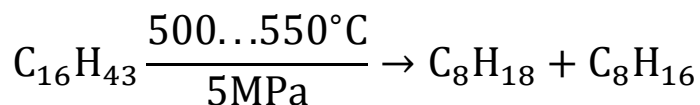
The use of cracking processes for oil processing allows to increase the yield of gasoline fractions.

**Cracking** – is a process of refining oil and its fractions, based on the decomposition (splitting) of complex hydrocarbon molecules under conditions of high temperatures and pressures.

Cracking was first proposed by scientist A.A. Litnij in 1875, and developed by V.G. Shukhov in 1891, but the first industrial plant was built in the USA.

There are the following **types of cracking**: thermal, catalytic, as well as hydrocracking and catalytic reforming.

**Thermal cracking** is used to obtain gasoline from fuel oil, kerosene, and diesel fuel.

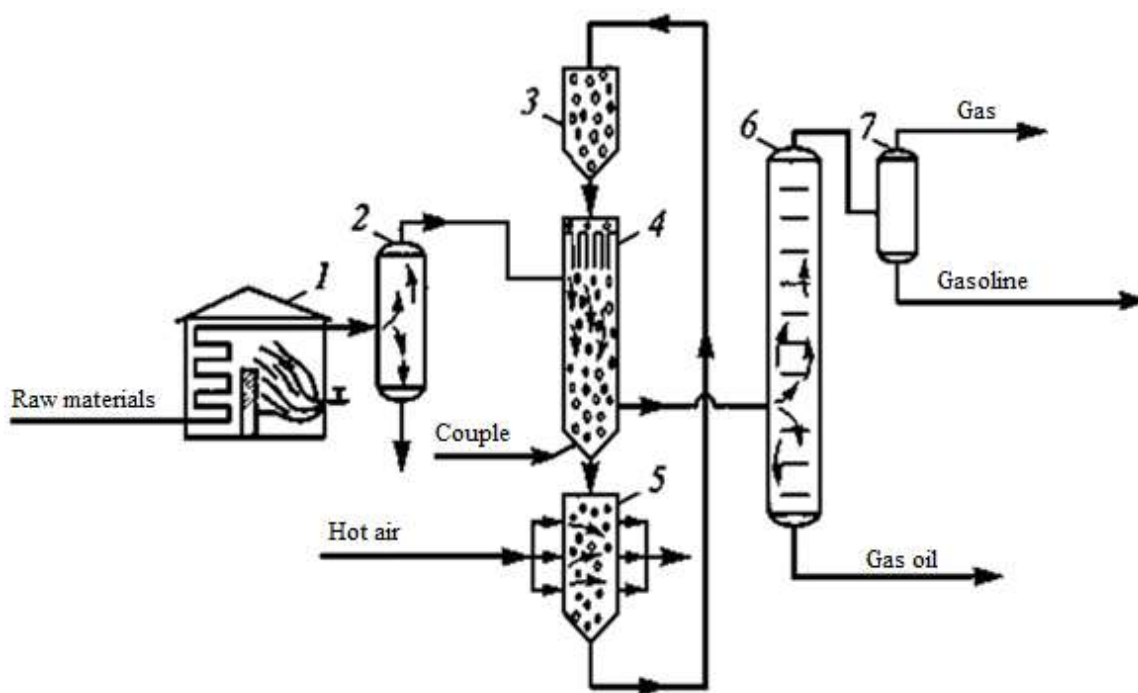


For example, when heated to 500...550°C under a pressure of 5 MPa, the hydrocarbon cetane, which is part of kerosene and diesel fuel, decomposes into normal octane and normal octene, which are components of gasoline, respectively.

Gasoline obtained by thermal cracking has an insufficiently high octane number (66...74) and a high content of unsaturated hydrocarbons (30...40%), that is, it has poor chemical stability, and it is used mainly only as a component when receiving commercial gasoline.

New installations for thermal cracking are currently not being built, since the gasoline obtained with their help oxidizes with the formation of resins during storage, and it is necessary to introduce special additives (inhibitors) into them, which sharply reduce the rate of tar formation.

**Catalytic cracking** – is a process of obtaining gasoline, based on the splitting of hydrocarbons and changing their structure under the influence of high temperature and a catalyst. Catalytic cracking at the plant was first implemented in 1919. N.D. Zelinsky.



1 – furnace for heating raw materials; 2 – evaporator; 3 – hopper with a catalyst; 4 – reactor; 5 – regenerator; 6 – rectification column; 7 – gas separator.

Figure 1.5 – Schematic diagram of catalytic cracking

As a raw material for catalytic cracking (fig. 1.5), gas oil and diesel fractions obtained during the direct distillation of oil are used, which are heated to a temperature of 450...525°C under a pressure of 0.15 MPa in the presence of an aluminosilicate catalyst, which accelerates the process of splitting molecules raw materials and isomerizes decomposition products, turning them into isoparaffinic and aromatic hydrocarbons. In this, the amount of olefins is reduced to 9...10%, and the octane numbers of the obtained gasolines, measured by the motor method, are equal to 78...85.

Catalytic cracking products are mandatory components during the production of A-80 gasoline.

**Hydrocracking** – is a process of oil product processing that combines cracking and hydrogenation of raw materials (gasoil, oil residues, etc.). This process is carried out under a hydrogen pressure of 15...20 MPa at a temperature of 370...450°C in the presence of aluminum cobalt molybdenum or aluminum nickel molybdenum catalysts.

Octane numbers of gasoline fractions obtained as a result of hydrocracking are 85...88 (according to the research method). Hydrocracking also increases the yield of light oil products – gasoline, diesel, and jet fuel.

As a raw material *for catalytic reforming*, gasoline fractions of primary oil distillation, boiling already at 85...180°C, are usually used.

Reforming is carried out in a hydrogen-containing gas environment (70...90% hydrogen) at a temperature of 480...540°C and a pressure of 2...4 MPa in the presence of a molybdenum or platinum catalyst.

Reforming when using a molybdenum catalyst is called *hydroforming*, and when using a platinum catalyst – *platforming*. The latter is currently used much more widely, as it is a simpler and safer process.

Catalytic reforming is used to obtain a high-octane component of automobile gasoline (85 according to the motor measurement method and 95 according to the research method).

**Oil production.** Under the influence of the ideas of D.I. Mendeleev oil producer V.I. Rogozin in 1876, built near Nizhny Novgorod the world's first oil production plant from fuel oil.

***Distillate and residual oils*** are distinguished by the production method.

When **distillate oils** are obtained, fuel oil is heated to 420...430°C (see Fig. 2), creating a vacuum column of 50 mm of mercury.

The yield of distillate oils from fuel oil is about 50%, the rest is **tar**.

**Residual oils** – are purified tars. To obtain them, fuel oil or semi-tar is mixed with liquefied propane (6...8 parts of propane per one part of fuel oil) at a temperature of 40...60°C. Aviation oils MK-22, MS-20 and transmission oil MT-16 are obtained in this way. MK-22 is also recommended for lubricating units of some cars.

Lubricants obtained from fuel oil, in addition to hydrocarbons, necessarily contain naphthenic acids, sulfur compounds and tar-asphalt substances, so they, like fuel, must be purified.

## **1.6 CLEANING OF FUELS AND OILS**

### **Fuel cleaning methods:**

1. To reduce the concentration of acidic products (organic acids, hydrogen sulfide), the distillate is treated with an alkali solution, and then washed with clean water.

2. To remove resins, the distillate is purified with sulfuric acid, and then washed successively with alkaline solutions and clean water.

3. Distillate with a high content of sulfur compounds is subjected to hydrogenation in the presence of a catalyst (hydrotreatment), as a result of which the sulfur content in the fuel is reduced by 10...20 times.

4. In the production of winter varieties of diesel fuels, paraffin hydrocarbons with high melting points are removed from them. The process of deparaffinization consists in mixing fuel with urea, which forms crystalline complexes with paraffins of normal structure, and its subsequent filtration. Fuel purified in this way retains fluidity down to minus 60°C.

### **Oil purification methods:**

1. Since the 70s of the 19th century, concentrated sulfuric acid, which dissolves resins and some sulfur compounds, and lye has been used for oil purification.

2. Bleaching clays are widely used for oil purification, on the surface of which resins, sulfur and organic acids and other substances are adsorbed. Most often, contact cleaning with the help of clay replaces the treatment of sour oil with alkali.

3. The selective method of purification using phenol and furfural produces oil with high chemical stability, i.e. raffinate oil, and tallow extract, which is used as an additive to transmission oils.

## **1.7 CONTROL QUESTIONS**

1. Name the elemental composition of oil.
2. What classes of hydrocarbons make up the bulk of oil?
3. How is direct distillation of oil carried out?
4. Tell about the secondary processes of oil refining.
5. How is the heat of combustion of fuel determined by its elemental composition?
6. What is called a lower heat of combustion?
7. How is the heat of combustion of liquid fuel determined by the research method?

## LECTURE 2. AUTOMOBILE GASOLINES (PART 1)

Lecture plan:

- 2.1 Introduction
- 2.2 Operational requirements for gasoline
- 2.3 Environmental properties of gasoline
- 2.4 Carburetion properties of gasoline
- 2.5 Low-temperature properties of gasoline
- 2.6 Control questions

### 2.1 INTRODUCTION

Motor transport is the main consumer of oil fuel.

Currently, there are about 1 billion cars in use in the world.

The car fleet of Ukraine is less than 1% of the number of cars in use in the world. At the same time, it is one of the most dynamically developing sectors of the global automotive market. Over the last decade, the number of cars in the country has increased by 1.7 times and continues to grow.

The total global consumption of motor fuels is about 1.75 billion tons/year, including automobile gasoline, which accounts for more than 800 million tons/year.

Until recently, it was believed that oil-based motor fuel would be actively replaced by alternative fuels: liquefied oil gas, compressed and liquefied natural gas, alcohols, hydrogen, electricity, etc.

However, the development of alternative types of fuels faces certain technical and economic difficulties, so there is confidence that liquid fuel of oil origin will remain the main source of both spark-ignition engines and diesel engines for the coming decades.

The assortment and quality of gasoline produced and used are determined by the structure of the country's automobile fleet, the technical capabilities of the domestic oil refining and petrochemical industry, as well as environmental requirements, which have recently become decisive.

The negative impact of motor vehicle emissions on the environment leads to the need to strengthen regulations on the composition of exhaust gases of cars.

Gasoline combustion products contained in the car's exhaust gases enter the atmosphere, polluting the environment. Particularly strong pollution of the air pool with these gases is observed in large cities with a large number of operated cars.

In order to reduce harmful emissions, cars were equipped with catalytic exhaust gas neutralization systems, and this, in turn, led to increased requirements for the quality of gasoline used.

Improving the design of engines and cars, improving the quality of gasoline produced and used, should be accompanied by a general increase in the culture of the operation of road transport.

### 2.2 OPERATIONAL REQUIREMENTS FOR GASOLINE

Gasoline is used as fuel for internal combustion engines with forced ignition. Gasoline is a mixture of hydrocarbons that boil at temperatures from 35 to 215°C.

Fuels for gasoline engines must have the following physical and chemical properties that will ensure:

- normal and complete combustion of the resulting mixture in engines (without detonation);
- formation of a fuel-air mixture of the required composition;
- uninterrupted supply of gasoline to the engine power system;
- absence of corrosion and corrosive wear of engine parts;
- the formation of deposits in the intake pipeline, combustion chambers and other parts of the engine as little as possible;
- preservation of quality during storage, pumping and transportation;
- formation of a minimal amount of combustion products that pollute the environment.

### 2.3 ENVIRONMENTAL PROPERTIES OF GASOLINE

They are provided with restrictions on the content of individual toxic substances according to the group hydrocarbon composition, according to the content of low-boiling hydrocarbons, as well as sulfur and benzene.

These restrictions allow for reliable operation of the exhaust gas neutralization catalytic system and contribute to reducing the impact of the car fleet on environmental pollution.

Table 2.1 shows the requirements for automobile gasoline in the countries of the European Economic Community.

Table 2.1 - Requirements for gasoline in the countries of the European Economic Community

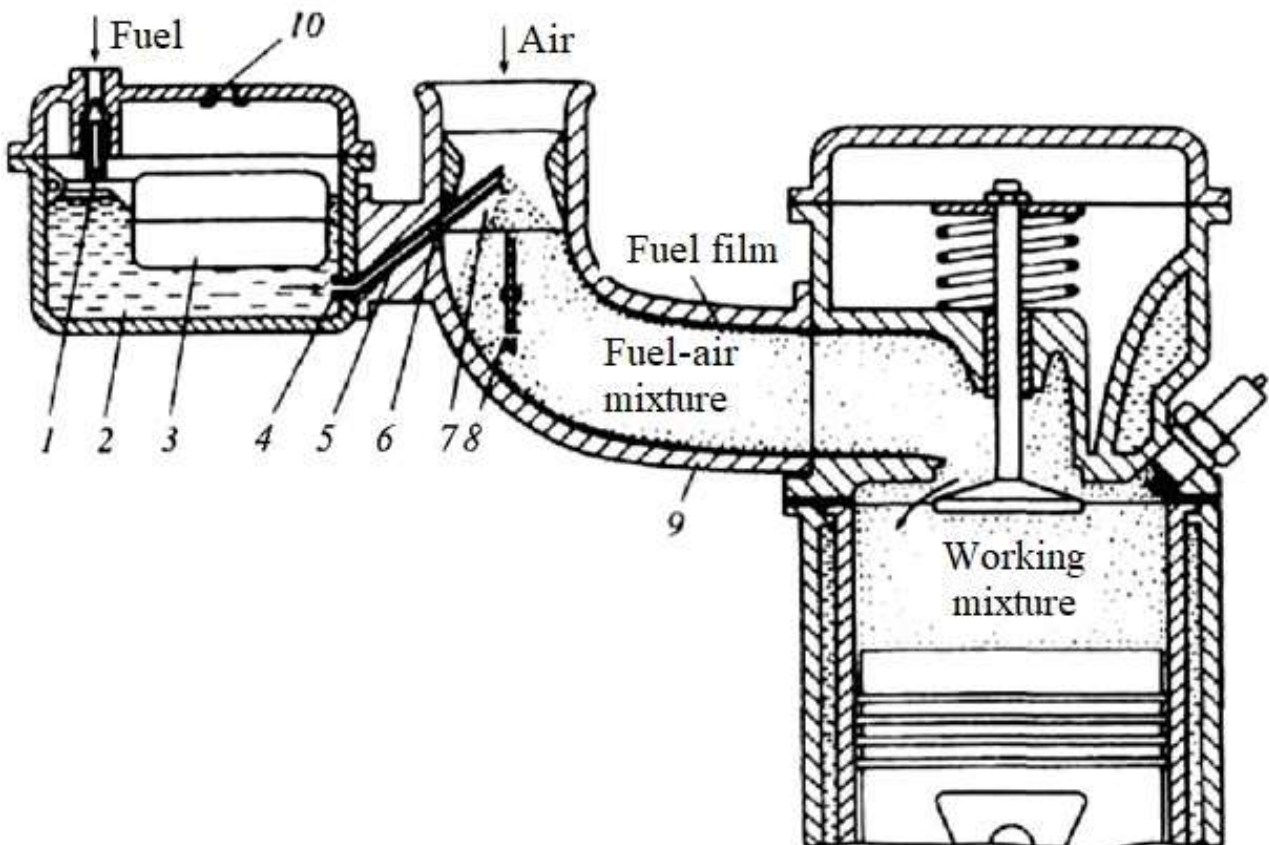
Indicator	Euro-2	Euro-3	Euro-4	Euro-5
Benzene content, max., %	5,0	1,0	1,0	1,0
Sulfur content, max. ppm	500	150	50	10
Content of aromatic hydrocarbons, max., %	–	42	35	35
Content of olefinic hydrocarbons, max., %	–	18	18	14
Oxygen content, max., %	–	2,3	2,7	2,7
Fractional composition:				
it is distilled to 100°C, no less	–	46	46	46
it is distilled to 150°C, no less	–	75	75	75
Saturated vapor pressure, kPa, no more	–	60	60	60
Presence of detergent additives	–	Necessarily		

In connection with the accession of Ukraine to European environmental programs, there was an urgent need to organize the industrial production of automobile gasoline that meets European requirements (EN-228).

## 2.4 CARBURETION PROPERTIES OF GASOLINE

Gasoline supplied to the fuel system of a spark-ignition engine forms a fuel-air mixture with air. This process is called *carburetion*. For complete combustion, it is necessary to ensure the homogeneity of the mixture with a certain ratio of gasoline vapors and air, the composition of the working mixture is determined by the carburetor dosing device. The formation of the working mixture occurs first in the carburetor mixer chamber and ends in the engine cylinders. The process of mixture formation lasts only 0.01...0.02 s.

Figure 2.1 shows the scheme of the simplest carburetor. Gasoline is supplied by the fuel pump to the float chamber - 2, the air cavity of which is connected to the atmosphere through hole 10. A constant level in the float chamber is maintained with the help of the float - 3 and the shut-off needle - 1. From the float chamber, gasoline through the jet - 4 is sucked into the mixing chamber due to the rarefaction created in the diffuser - 6 during the intake stroke. The maximum fuel consumption occurs when the throttle valve is fully opened - 8. In the intake pipe - 9, gasoline breaks up into small droplets, the average diameter of which is 0.1-0.2 mm and evaporates. The mode of gasoline evaporation begins in the carburetor, continues in the intake pipeline and ends in the engine cylinders. But some of the gasoline drops leaving the carburetor diffuser settle on the walls of the intake pipe and form a film of liquid fuel, which leads to uneven distribution of the mixture in the cylinders.



1 – needle valve; 2 – float chamber; 3 – float; 4 – jet; 5 – atomizer; 6 – diffuser; 7 – mixing chamber; 8 – throttle valve; 9 – intake pipeline; 10 – hole in the float chamber.

Figure 2.1 – Scheme of the simplest carburetor

The process of forming a mixture of the required composition can be represented schematically as follows:

- from the float chamber of the carburetor, due to the pressure difference, the fuel passes through the jets that dose its amount, and flows out of the atomizer located in the mixing chamber;
- the leaking fuel is dispersed into small droplets in the air stream, which is sucked into the engine cylinders through the carburetor mixing chamber;
- the evaporation of the atomized fuel, which continues in the intake pipeline of the engine, begins; At the same time, fuel and air vapors mutually diffuse, forming a fuel-air mixture.

The improvement of external mixing systems has led to the creation of various designs of new type power supply devices with gasoline injection through electromagnetic nozzles directly into the intake manifold. In such power systems, compared to carburetor engines, the uniformity of the distribution of the fuel mixture among the cylinders is ensured, the intake resistance is reduced and the filling of the cylinders is improved, a more flexible correction of the mixture composition is achieved when the engine operating mode is changed, and the prerequisites are created for optimal engine control at all modes using microprocessor technology. Due to this, the fuel efficiency indicators are improved by 12-18% compared to traditional carburetor systems. In addition, there is a sharp decrease in the content of a number of harmful substances in exhaust gases. As a result, the power system with gasoline injection is increasingly used, despite the higher cost and complexity of operation.

The following physicochemical parameters of the fuel have the greatest influence on the process of formation of a working mixture of the required composition: ***density, viscosity, fractional composition, saturated vapor pressure***.

**Fuel density.** Density, as you know, means the mass of a substance per unit volume. In the CI system, density is measured in kg/m<sup>3</sup>, but in practice other units are still used - g/cm<sup>3</sup>, kg/l. The density of gasoline (as well as its viscosity) affects fuel consumption through the calibrated holes of the carburetor jets. The level of gasoline in the float chamber depends on the density. Therefore, the density value for automobile gasoline at a temperature of +20°C should be within 690-780 kg/m<sup>3</sup>. The use of gasoline with a significantly reduced density can lead to an increase in its level in the float chamber of the carburetor and involuntary leakage of fuel from the atomizer.

Since fuels with the same density, but of different origin and chemical composition, have different properties, the density as such does not characterize their properties.

Fuel density is determined by a hydrometer, hydrostatic scales, and a pyknometer. Due to the simplicity and speed of determining the density with a hydrometer, this method is used most often, although it is less accurate than the other two.

Knowing the temperature at which the density was determined, it can be brought to the standard temperature (+20°C) using the formula:

$$\rho_{20} = \rho_t + \gamma(t - 20).$$

where  $\rho$  – is the density of the tested product at the test temperature, kg/m<sup>3</sup>;  $t$  – test

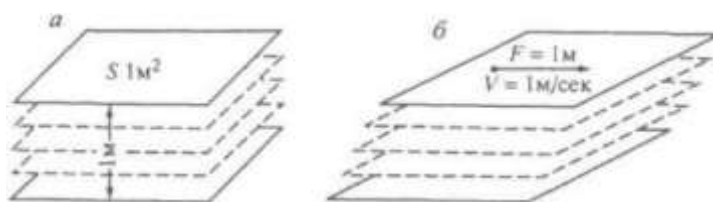
temperature, °C;  $\gamma$  – temperature correction of density (determined according to the calculation table, varies within 0,515-0,910 kg/m<sup>3</sup>).

**Gasoline density increases by approximately 1% for every 10°C decrease in temperature.**

**Viscosity** (internal friction) is a property of liquids that characterizes resistance to the action of external forces that cause their flow. Fuel viscosity depends on temperature, chemical composition and structure of hydrocarbons.

The value of viscosity can be expressed in absolute units of dynamic and kinematic viscosity or conventional units. In the CI system, the unit of dynamic viscosity ( $\eta$ ) is the viscosity of such a liquid that resists the mutual displacement of two layers of liquid with an area of 1 m<sup>2</sup>, located at a distance of 1 m from each other and moving with a relative force of 1N at a speed of 1 m/s (fig. 2.2).

Dynamic viscosity is determined in a capillary viscometer or in a rotary viscometer RV-7. When determining the dynamic viscosity in a capillary viscometer, the time to the end of liquid outflow through the viscometer capillary under the action of a certain pressure (not lower than 13.3 kPa) is measured. Dynamic viscosity is calculated using the following formula:  $\eta = \nu \cdot \rho$



a) initial position, b) moment of displacement

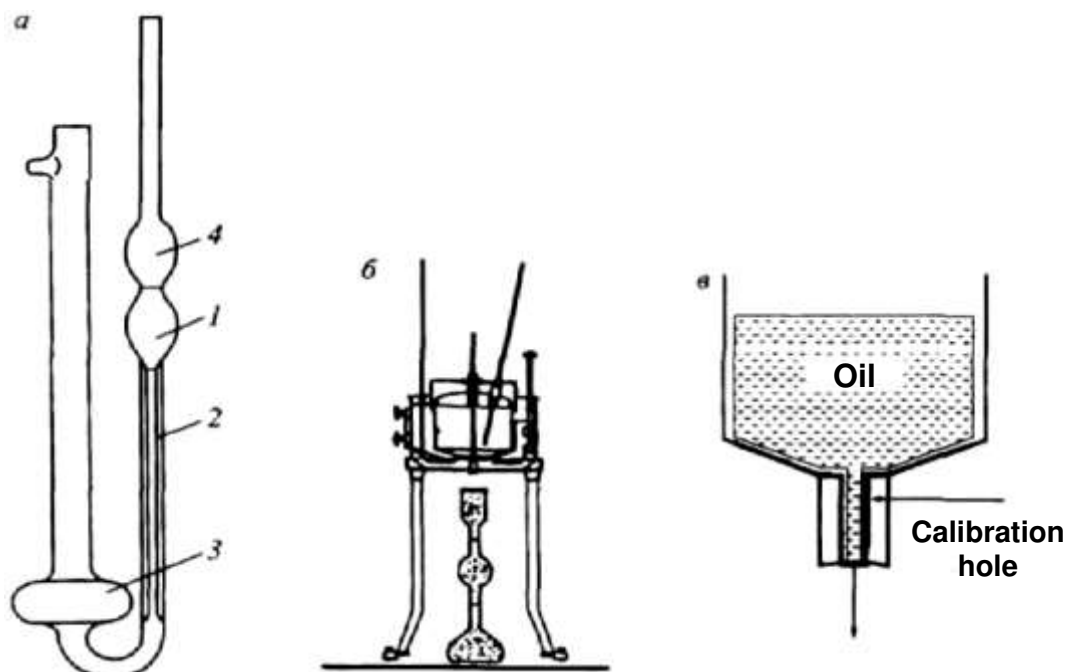
Figure 2.2 – The scheme for determining the unit of dynamic viscosity

**Kinematic viscosity** – it is the dynamic viscosity divided by the density of the liquid determined at the same temperature at which the viscosity was determined. Knowing the value of the dynamic viscosity, the kinematic viscosity is determined by the formula:

$$\nu_t = \frac{\eta_t}{\rho_t}$$

where  $\nu_t$  – kinematic viscosity;  $\eta_t$  – dynamic viscosity;  $\rho_t$  – density.

According to the current measurement system (CI), the unit of dynamic viscosity ( $\eta$ ) is Pa•s (Pascal-second), and of kinematic ( $\nu$ ) m<sup>2</sup>/s. In the old measurement system (SGS), the unit of dynamic viscosity was 1 P (poise), and kinematic viscosity was 1 St (Stokes). The relationship between the SGS and SI systems is as follows – for dynamic viscosity 1P (poise) = 0,1 Pa•s, and a hundredth part of 1 cP (centipoise) = 1 mPa•s, for kinematic viscosity – 1 St ( stokes) = 1 SI m<sup>2</sup>/s = 1 cm<sup>2</sup>/s, hundredth part of stokes 1 cSt (santistokes) = 1 mm<sup>2</sup>/s.



a) Pinkevich's capillary viscometer (1, 3, 4 - expansion volumes, 2 - capillary); b) viscometer for determining conditional viscosity (Engler viscometer); c) scheme of leakage of petroleum products through the calibration hole.

Figure 2.3 – Viscometers of various types

The definition of kinematic viscosity is based on the measurement of the time it takes for a certain volume of liquid to flow under the influence of gravity at a given temperature. The most common determination of kinematic viscosity is by means of capillary viscometers (fig. 2.3).

This method is based on the fact that the viscosity of liquids is directly proportional to the time of flow of the same quantities through the same capillary, which ensures laminar flow. The viscometer is calibrated using liquids whose viscosity is precisely known. To maintain the temperature at which the viscosity is determined, the viscometer is placed in a thermostat or in a water bath. The time of the end of the flow of the oil product through the calibration hole is determined. Knowing this time, the kinematic viscosity is calculated using the formula:

$$v_t = C \cdot \tau$$

де  $C$  – constant viscometer,  $\text{mm}^2/\text{s}$ ;  $\tau$  – time of leakage of the oil product through the capillary, s.

Sometimes the conventional viscosity is determined.

**Conventional viscosity** – is the viscosity expressed in conventional units obtained in various viscometers. It is customary to express conditional viscosity in degrees VU (conditional viscosity), which correspond to degrees of Engler.

The viscosity of automobile gasoline at a temperature of  $+20^\circ\text{C}$  can be in the range from 0,5 to 0,7  $\text{mm}^2/\text{s}$ .

When the temperature of gasoline changes, its density and viscosity change.

When the temperature of gasoline decreases, its density increases, which leads to an increase in fuel consumption. A decrease in temperature simultaneously causes an increase in the viscosity of gasoline, which leads to a decrease in its consumption.

Viscosity has the greatest effect on reducing consumption in the total effect of changes in viscosity and density of gasoline. Viscosity also has a predominant effect on the weight amount of fuel flowing through the calibrated orifice per unit of time. Gasoline consumption through the calibrated hole is reduced by 20-30% when the temperature changes from 40 to -40 °C.

**Surface tension.** The degree of atomization of gasoline is influenced primarily, in addition to viscosity, by surface tension: the smaller their size, the smaller the resulting drops. The value of surface tension is characterized by the work required for the formation of 1 m<sup>2</sup> of liquid on the surface (that is, for the movement of liquid molecules from its volume to a surface layer with an area of 1 m<sup>2</sup>) and is expressed in N/m.

**Volatilization of fuel.** Volatilization of fuel is understood as its ability to change from a liquid state to a gaseous state.

Automotive gasoline must have such a volatility that ensures easy starting of the engine, its quick heating and complete combustion of gasoline after that, and also excludes the formation of steam plugs in the fuel system.

The speed and completeness of the transition of fuel from liquid to gaseous state under these conditions are determined by its chemical composition and depend on external conditions (temperature, speed of gas flow, etc.). Since these conditions are not the same in different engines, the requirements for fuel evaporation are related to the design of the engine for which it is intended. Combustion is always preceded by evaporation of liquid fuel and mixing of its vapor with air to form a combustible mixture. With poor evaporation, part of the fuel does not turn into a gaseous state and burns.

A distinction is made between static (from a stationary surface into stationary air) and dynamic (fuel and air moving relative to each other) evaporation of fuels.

Static evaporation manifests itself primarily during the storage of petroleum products in tanks, and with a greater speed, the lower the external pressure, the higher the temperature of the petroleum product and the environment, the pressure of saturated vapors, the coefficients of diffusion, thermal conductivity and heat capacity, the heat of evaporation and the larger the size of the tank. The speed of dynamic evaporation (it is most pronounced during the preparation of fuels for combustion in engines) is affected by the same factors as in static evaporation, but the factor of the movement of the media relative to each other and the degree of atomization of the fuel affect it to a greater extent.

The evaporation of fuels can be judged (albeit approximately) by the density and boiling point of hydrocarbons. In practice, the volatility of engine fuels is assessed by determining their fractional composition (for gasoline, the saturated vapor pressure is also measured).

**The fractional composition** of oil (petroleum) products is the content of certain fractions in them, expressed in volume or mass percentages, which is determined for gasoline and diesel fuels on a standard device for distilling petroleum products. Gasoline, being a mixture of hydrocarbons, does not have a fixed boiling point: it evaporates in the temperature range of 35-215°C.

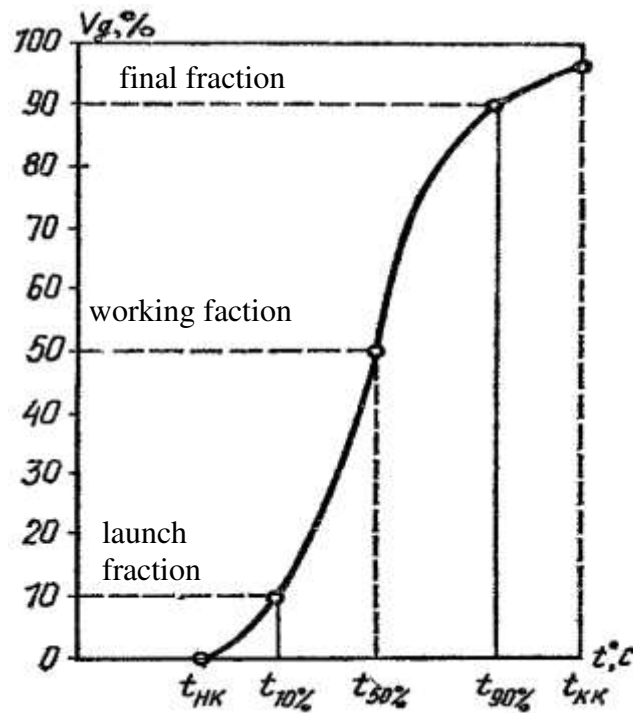


Figure 2.4 – Fractional composition of gasoline

When determining the fractional composition, gasoline (100 ml) is heated in a special device, and the resulting vapors are cooled. Condensing, they turn into a liquid, which is collected in a measuring cylinder. The temperatures of the beginning of boiling are fixed - the first drop falling into the cylinder, the boiling of 10, 50, 90% of the fuel and the end of boiling.

The characteristic temperature points of the acceleration of the fuel are given in the standards and quality passports, based on these points, in particular, the operational qualities of gasoline are evaluated.

**Light fractions of gasoline**, characterized by the interval on the curve (Fig. 2.4) from the beginning of boiling to the boiling point of 10%, determine the starting properties of the fuel: *the lower the boiling temperature of 10% of the fuel, the better they are*. To start a cold engine, it is necessary that 10% of gasoline be boiled at a temperature not higher than 55°C (winter grade). Based on the boiling point of 10%, the minimum temperature of the surrounding air at which the engine can be started can be approximately determined by the formula:

$$t_B \geq 0,5 \cdot t_{10\%} - 50,5.$$

If the ambient air temperature is below minus 25-30 °C, starting a cold engine without preheating or using special starting fluids is difficult. When using a winter type of gasoline in the summer, light fractions begin to evaporate intensively in the fuel tank and gas lines, the filling ratio of the cylinders decreases, power drops, the engine overheats, and steam plugs form in the fuel system, interruptions occur, the engine stalls. Therefore, the amount of low-boiling hydrocarbons in summer grade gasoline is limited.

*The quality of the combustible mixture* at different engine operating modes, *the duration of the warm-up* (transition from idling to the operating mode), *receptivity* (the possibility of a quick transition from one mode to another) *depend on the evaporation of the working fraction* (on the acceleration curve from 10 to 90%), which standard is normalized by a 50% point. *The lower the temperature of this point, the more homogeneous the composition of the working mixture in individual cylinders, the more stable the engine works, and its efficiency improves.*

*The boiling point of 90% of the fuel*, which characterizes its tendency to condensation, is usually *called the dew point*. The tendency of fuel to condense is less, the shorter the temperature interval from 90% to the final boiling, when heavy hydrocarbons evaporate. Since heavy hydrocarbons do not evaporate completely, remaining in a droplet state, they can penetrate through the gaps between the cylinder and the piston rings into the engine crankcase, which leads to the washing of the lubricating film, increased wear of parts, thinning of the oil, and increased fuel consumption. Therefore, it is believed that the smaller the temperature interval from 90% to the end of boiling and, therefore, the tendency of fuel to condense, the higher its quality, better economy and lower rate of wear of engine parts.

**Saturated vapor pressure.** The presence of the lightest fractions in the fuel, which affect the start of the engine and the formation of steam plugs in the fuel system, is additionally determined by the "*saturated vapor pressure*" indicator. The higher this indicator is, the faster and more fully the gasoline evaporates and the easier it is to start the engine (fig. 2.5). Therefore, it should be higher for winter types of gasoline than for summer ones.

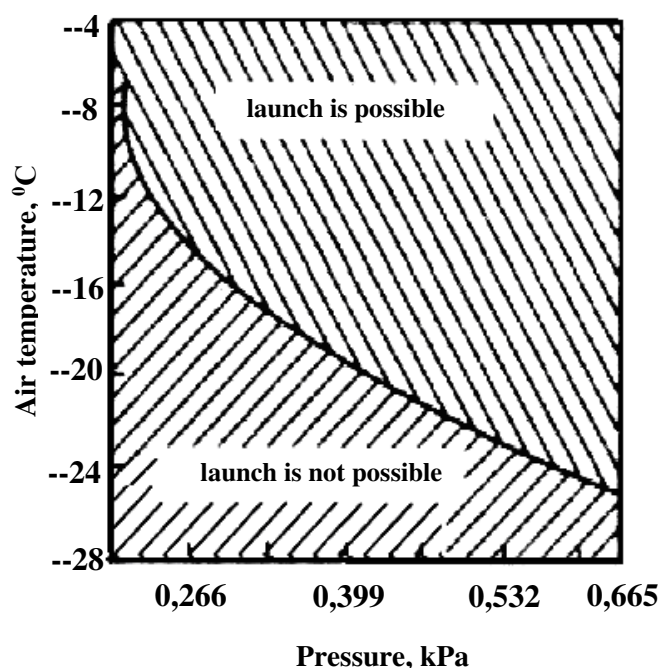


Figure 2.5 – The effect of saturated gasoline vapor pressure on the minimum engine start-up temperature

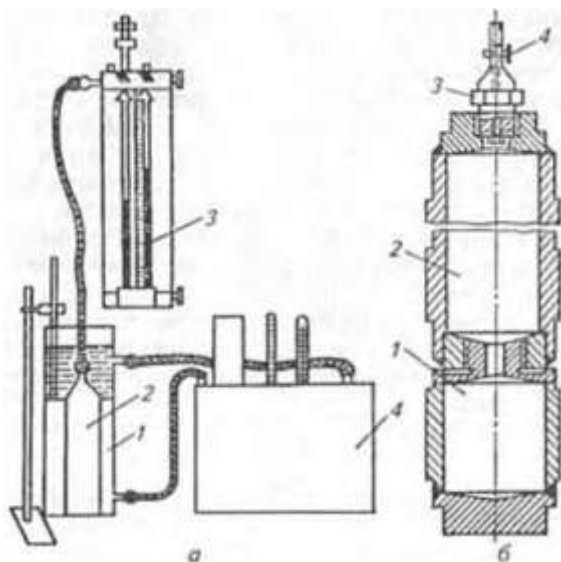
Under *the pressure of saturated vapors* of liquid fuel, we mean the pressure of vapors that are in equilibrium with the liquid at a given temperature and a certain ratio of the volumes of the liquid and vapor phases. The more light fractions in gasoline, the higher the pressure of saturated vapors.

The tendency of gasoline to form vapor jams, its possible losses during storage, transportation and refueling of the car, and the ease of starting the engine depend on the pressure of saturated vapors. The more low-boiling hydrocarbons in gasoline, the higher its evaporation rate and saturated vapor pressure, and therefore the tendency to form vapor plugs.

The higher the vapor pressure during fuel evaporation in a closed space, the more intensive their condensation process. The vapor pressure of evaporating gasoline on the walls of the container is called *vapor elasticity*, which depends on the chemical and fractional composition of gasoline. The elasticity (pressure) of vapors increases with increasing temperature. It is higher because it contains more low-boiling hydrocarbons in the fuel.

The standard limits the upper limit of vapor pressure to 670 Pa in summer and from 670 to 930 Pa in winter, as gasolines with high vapor elasticity are prone to increased formation of vapor plugs in the fuel system; their use causes a decrease in cylinder filling, a drop in power.

Limiting the pressure of saturated steam is due to an increase in the probability of formation of steam plugs in the engine power supply system, especially in the summer period of operation.



*a* – scheme of the device: 1 – water bath; 2 – bomb; 3 – mercury manometer; 4 – thermostat;  
*b* - bomb device: 1 and 2 - fuel and air chambers. 3 – nipple; 4 – gas tap.

Figure 2.6 – Device for determining the pressure of saturated vapors by the standard method

Saturated vapor pressure is determined by the Reid method (ISO 3007-99). The essence of the method is to measure the pressure of saturated fuel vapors in a two-chamber bomb at a temperature of 37.8°C. The scheme of the device is shown in figure 2.6, a. A metal bomb consists of a fuel chamber 1 (fig. 2.6, b) with one hole and an air chamber 2, which are connected using a thread. The volume ratio of the wind and fuel chambers is 3.95:4.05. In the upper part of the air chamber there is a nipple 3 with a gas valve 4 and a tip of a rubber tube.

Pressure is measured with a mercury or spring manometer. Mercury manometer 3 (see fig. 2.6, a) is a U-shaped glass tube filled with mercury. A rubber tube is put on one end of the manometer, which is then connected to the air chamber of the bomb.

When conducting tests, the assembled apparatus is overturned. At the same time, the gasoline in the fuel chamber flows into the air chamber. Then the apparatus is strongly shaken several times in a direction parallel to the axis. Next, the device is returned to its normal position and immersed in a water bath, while the faucet must also be in the water. The temperature of the bath is maintained at 37.8 °C. The device is kept in the bath for 5 minutes. Then it is taken out of the bath, turned over, shaken vigorously along the axis and put back into the bath. The removal and shaking operation is repeated after 5 minutes of exposure, then the device is placed in the bath again. After 2 minutes, open the gas tap and record the readings of the manometer. Tests continue until two consecutive readings are the same. The duration of the test is usually 20...30 minutes. The final reading of the manometer is taken with an accuracy of 1 kPa.

When calculating the pressure of saturated gasoline vapors, a correction is made to the readings of the manometer for the change in the pressure of air and saturated water vapor in the air chamber, caused by the difference between the initial air temperature and the temperature of the water bath.

## 2.5 LOW-TEMPERATURE PROPERTIES OF GASOLINE

The *low-temperature properties* of gasoline determine their ability to ensure the performance of the fuel system at negative temperatures.

At low temperatures, the supply of gasoline to the engine may stop due to the fall of ice crystals or the formation of ice deposits on the parts of the fuel system. Since the vast majority of hydrocarbons included in gasoline solidify at very low temperatures, and the solidification temperature of automobile gasoline is usually lower than minus 60 °C, this indicator is not regulated for them. The biggest complications when operating engines at low temperatures are associated with the formation of ice crystals in gasoline. Gasoline in a dissolved state may contain only a few hundredths of a percent of water. It was established that the solubility of water in gasoline decreases as the temperature decreases. With high air humidity and positive temperatures, the water content even in dehydrated gasoline increases sharply almost instantly. During rapid cooling of gasoline, excess moisture, which did not have time to pass into the air, is released in the form of small droplets, which turn into ice crystals at negative temperatures. By clogging the filters, the crystals disrupt the supply of gasoline to the engine.

*The more aromatic hydrocarbons in gasoline, the higher the water solubility.* Benzene is the most hygroscopic. Therefore, from the point of view of reducing the danger of ice crystal formation when cooling gasoline, *the content of aromatic hydrocarbons* in them, and in particular benzene, *should be limited*.

Additives are added to gasoline to prevent the formation of ice crystals.

Water can be in gasoline and in the form of a second phase: it must be separated from gasoline and drained.

## **2.6 CONTROL QUESTIONS**

1. What are the operating requirements for gasoline?
2. How do the density and viscosity of gasoline affect its consumption?
3. What indicators are used to evaluate the volatility of gasoline?
4. What effect does the evaporation of gasoline have on the operation of the engine in different climatic conditions?
5. What is the fractional composition of gasoline?
6. Define the term "saturated vapor pressure".
7. Why low-temperature properties of gasoline are needed&

## LECTURE 3. AUTOMOBILE GASOLINES (PART 2)

Lecture plan:

- 3.1 Normal and detonation combustion.
- 3.2 Detonation resistance of gasoline and its evaluation. Anti-detonators.
- 3.3 Gasoline properties affecting the formation of deposits in the engine.
- 3.4 Corrosion properties of gasoline.
- 3.5 Environmental requirements for gasoline.
- 3.6 Control questions.

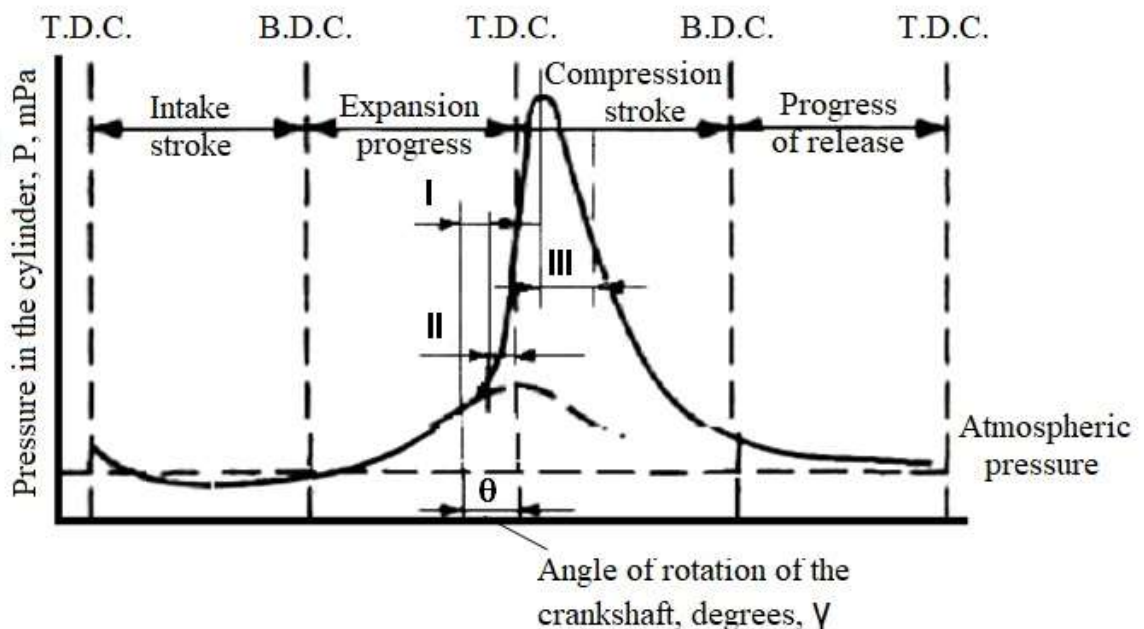
### 3.1 NORMAL AND DETONATION COMBUSTION

Increasing the power and efficiency of gasoline engines is possible primarily due to an increase in the compression ratio. This trend makes it possible to fully improve engine designs. At the same time, it imposes stricter requirements on the detonation resistance of gasoline: the higher the detonation resistance, the more economical and efficient the engine is.

When fuel is burned in the engine, its chemical energy is converted into thermal energy and then into mechanical energy. The nature of the combustion process determines both the engine's power and economic performance, as well as its reliability and durability.

***The type of combustion in the engine can be divided into normal and abnormal.***

During the normal working process in the engine with spark ignition, the combustion of the mixture can be conditionally divided into three phases (fig. 3.1): I – the initial one, during which a small combustion center that appears between the spark plug electrodes gradually turns into a developed turbulent flame front; II – the main phase of flame propagation; III – phases of afterburning of the mixture.



*I, II, III - duration, respectively, of the initial, main and final phases of combustion in degrees of rotation of the crankshaft;  $\theta$  - ignition advance angle.*

Figure 3.1 – Indicator diagram of the combustion process in a spark ignition engine

It is impossible to draw a sharp line between individual phases of combustion, since the nature of the process changes gradually.

**The first phase** – the period of hidden combustion or the period of ignition delay (12-15% of the total fuel combustion time) is characterized by a more intense preparation of the working mixture for combustion than in the compression period. In this phase of combustion, oxidation processes are intensified (primarily due to the heating of the mixture from the electric spark, low-temperature combustion of fuel occurs), and the increase in pressure practically does not differ from the increase in pressure caused by compression without combustion.

**The second phase** – direct combustion (accompanied by a faster than pure compression pressure increase) continues until the maximum pressure rise and usually ends a few degrees after top dead center (T.D.C.). Combustion takes place more intensively at a higher temperature of the working mixture at the moment of the spark. The burning rate is subject to the law of effective masses:

$$v = kC_1C_2C_3,$$

where  $v$  – reaction rate;  $C_1, C_2, C_3$  – concentration of active substances;  $k$  – constant, which depends on the nature of the reactants.

Since the rate of combustion is proportional to the product of the concentrations of the reactants, as combustion proceeds, when their concentration decreases, the rate of combustion decreases.

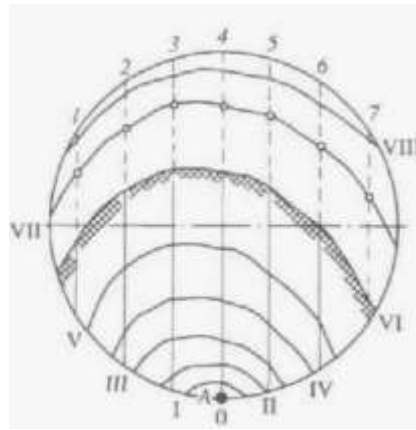
The chemical composition and amount of fuel, its ratio with air, the amount of residual gases in the cylinder, the temperature and pressure of the mixture, the design of the combustion chamber and a number of other factors significantly affect the rate of combustion. The most intensive combustion process occurs at  $\alpha=0.95$ , which is characteristic of a small enrichment of the combustible mixture. Further enrichment of the fuel leads to an increase in the incompleteness of its combustion, and depletion – heat consumption for heating excess nitrogen. In both cases, the burning rate decreases. When the compression ratio of the engine increases, the combustion process intensifies (the temperature and pressure of the mixture increase).

**The normal course** of the process is illustrated by the diagram of the combustion of the working mixture and the spread of the flame front shown in fig. 3.2.

It can be seen that the combustion rate is approximately constant throughout the entire period, the pressure in the engine cylinder from the expanding combustion products increases smoothly and reaches a maximum value near the T.D.C., the piston moves down (to the B.D.C.), and occupied the volume increases with combustion products. All this characterizes the normal operation of the engine.

During normal combustion, the process proceeds smoothly with an almost complete course of fuel oxidation reactions and an average flame propagation speed of 10-60 m/s.

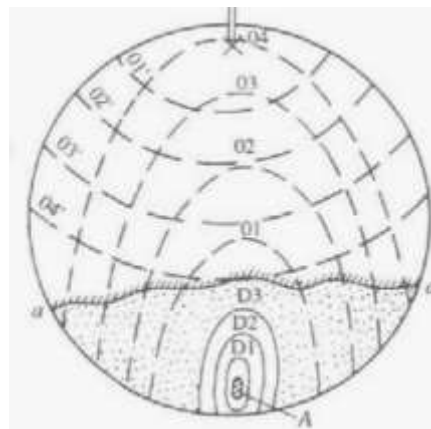
**The main disturbances of normal combustion in an engine with ignition from a spark are: detonation, premature and subsequent ignition (larynx ignition), ignition from compression when the ignition is turned off.**



*A - spark*

Figure 3.2 – Scheme of the flame front spread across the combustion chamber

**Detonation occurs** when part of the fuel-air mixture spontaneously ignites, to which the flame from the candle reaches last. Externally, detonation manifests itself in the occurrence of resounding metal knocks when the engine is operating at high loads. The speed of flame propagation increases sharply (almost 100 times) and reaches 1500-2500 m/s, detonation combustion occurs, which is characterized by an uneven course of the process, a sudden change in the speed of flame movement and the appearance of a shock wave (fig. 3.3).



*A - center of self-ignition (detonation); D1-D3 - instantaneous positions of the spread of the burning zone from the hearth A; O1-O4 - shock waves; O1'-O4' - reflected waves; a-a - position of the flame front.*

Figure 3.3 – Physical picture of detonation combustion in an engine

Oxidation reactions do not take place completely in exhaust gases, products of incomplete combustion of fuel are found. Detonation leads to a loss of engine power due to incomplete combustion (fig. 3.4).

At the same time, the temperature of the cylinder heads and coolant rises sharply, and smoke appears in the exhaust gases. Long-term operation with detonation leads to overheating of the engine, as a result of which premature self-ignition of the working mixture may occur, as well as mechanical damage to individual parts of the engine (fig. 3.5).

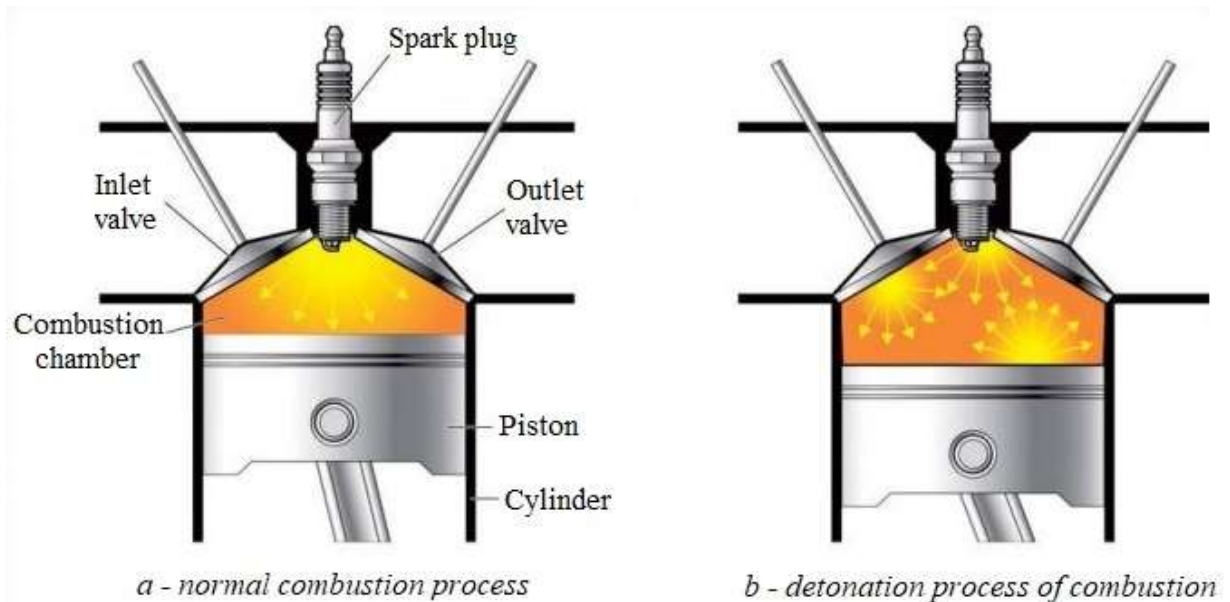


Figure 3.4 – The combustion process of the fuel-air mixture in the combustion chamber

Burnout of pistons and valves, burning of piston rings, violation of candle insulation, cracking of connecting rod bearing liners – all this can be caused by detonation. According to the peroxide theory (it is now generally accepted), during detonation, the primary products of fuel oxidation are formed – organic peroxides.



Figure 3.5 – Engine parts destroyed by detonation

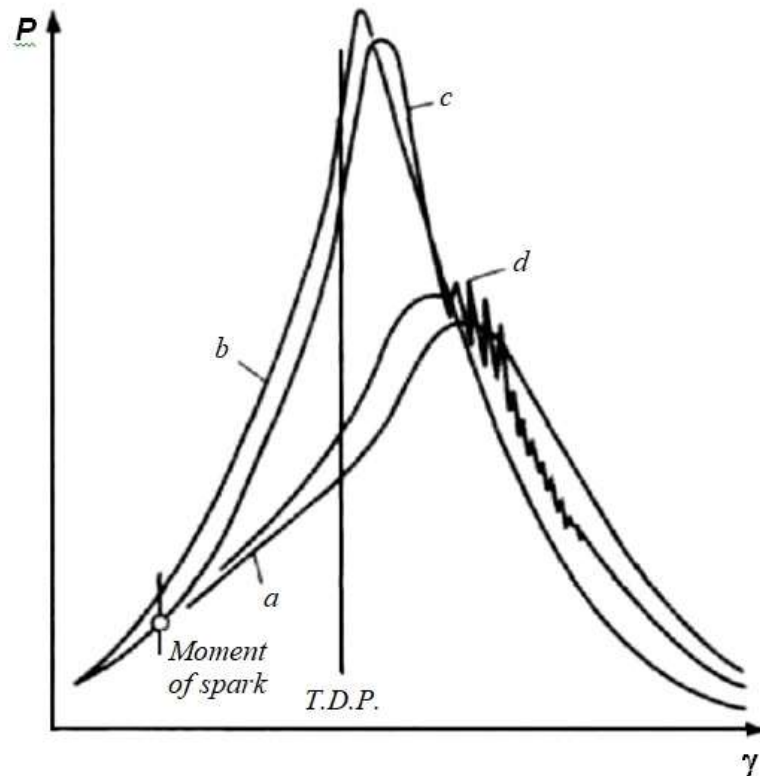
When an oxygen molecule is attached to hydrocarbons, the C-C bond forms peroxide ( $R-O-O-R$ ), and the C-H bond forms hydroperoxide ( $R-O-O-H$ ).

Peroxides formed in the process of preliminary oxidation, accumulating in the unburned part of the working mixture, disintegrate (upon reaching a critical concentration) with an explosion and release of a large amount of heat. This activates the whole mixture. Such a moment will be accompanied by explosive combustion of the mixture, that is, detonation. Figure 3.6 shows an indicator diagram taken during engine operation with detonation.

The most favorable place for the occurrence of a detonation wave (detonation focus) is a part of the gasoline-air mixture located in remote parts of the combustion chamber.

From the focus of detonation, the combustion spreads quickly throughout the entire part of the fuel-air mixture and covers it.

The mechanism of propagation of the combustion wave from the detonation center is different from the mechanism of normal combustion. ***The flame front in the detonation wave does not propagate through heat transfer, but due to the instantaneous release of a large amount of chemical energy in a small volume.*** This causes a sharp local increase in pressure, resulting in a shock wave. The latter, passing at a speed of up to 2500 m/s along the remaining unburned part of the mixture, causes its compression, heating and ignition. The detonation wave is repeatedly reflected from the walls of the cylinder, causing a characteristic metallic knock.



*a - normal combustion; b, c - glow ignition; d - detonation combustion;  
P - pressure;  $\gamma$  - crankshaft turning angle.*

Figure 3.6 – Indicator diagram of the main types of fire in an engine

The following ***groups of factors*** affecting the occurrence and intensity of detonation are distinguished: depending on the engine design, operational and related to fuel properties.

***Design factors*** affecting the combustion process are the degree of compression, the shape and dimensions of the combustion chamber, the number and location of candles, the diameter of the cylinder, the stroke of the piston, the material of the engine cylinder head.

***Operational factors*** affecting the occurrence of detonation are the air excess ratio, engine speed, ignition advance angle, coolant temperature, air humidity, soot layer in the combustion chamber, and others.

***A factor related to fuel properties is its detonation resistance.*** Moreover, when the fuel evaporates in the process of mixture formation (due to the different detonation resistance of individual fractions), detonation can also increase. The detonation resistance of gasoline depends on its hydrocarbon composition. Aromatic hydrocarbons have the highest detonation resistance, isoparaffinic and olefinic hydrocarbons have the lowest detonation resistance, and paraffin hydrocarbons have the lowest.

When about 5% of the mixture detonates, external signs of detonation appear. If 10-12% of the mixture detonates, detonation of medium intensity is observed. Very strong detonation is characteristic of 18-20% of the detonating mixture. Detonation fuel combustion is characterized by a characteristic sharp metallic knocking in the cylinders, overheating of the cylinder heads and a drop in its power, which periodically appears as black smoke from exhaust gases. Detonation leads to burnout of pistons, exhaust valves, engine overheating.

One of the most common types of abnormal combustion is *glow ignition*.

*The glow ignition* refers to uncontrolled ignition of the working mixture from a hot body: smoldering carbon or overheated parts.

The peculiarity of ignition with smoldering soot is its relationship with detonation: when detonation waves occur, soot is partially removed from the walls of the combustion chamber, thereby eliminating glow ignition, because hot spots disappear – the cause of spontaneous ignition of the working mixture. Since the rate of combustion of the mixture increases, detonation stops, but after the emission of soot particles, it resumes again.

In the case of glow ignition with overheated parts (central electrodes, "skirts" of candle insulators, less often exhaust valves), the ignition does not stop as it burns out, but progressively self-intensifies.

To assess the propensity of candles to overheat, an indicator called the glow number (GN) is used. Its value for this engine is selected so that, on the one hand, the possibility of flash ignition at heat-stressed modes is excluded (in this case, a low GN is required), and on the other hand, to ensure that the temperature of the edge of the "skirt" and the central insulator is not lower than 397°C at the minimum modes in order to avoid their coking (for this, a sufficiently high GN is required). The activity of soot from the point of view of glow ignition depends on the content of aromatic hydrocarbons and ash additives in gasoline. Since high-molecular aromatic hydrocarbons form an active soot prone to self-heating (the presence of tetraethyl lead (TEL) combustion products in the soot lowers the soot ignition temperature from 550-600 to 200-300 °C), it is especially difficult to meet these requirements in fuels with high detonation properties.

The glow ignition is combated by improving the design of the combustion chambers and changing the properties of the soot formed by introducing special additives into the fuel.

### **3.2 DETONATION RESISTANCE OF GASOLINE AND ITS EVALUATION. ANTI-DETONATORS.**

One of the main indicators of the quality of automobile gasoline is their detonation resistance, which largely depends on the reliability, power increase, economy and service life of the car engine.

The development of methods for evaluating the anti-knock properties of gasoline began in 1918-1919, almost simultaneously with the study of the detonation phenomenon in engines, when G. Ricardo created an engine with a variable compression ratio and proposed to evaluate fuel by the value of the compression ratio at which the engine develops maximum power. This figure was called the highest useful compression ratio.

Further research showed the failure of the method, as the value of the highest useful compression ratio did not remain constant when switching to another engine, but also changed even when working on the same engine, depending on the environmental conditions.

Later, a method of assessing the detonation resistance of fuel using fuel equivalents was developed, based on a comparison of the anti-knock qualities of the tested fuel with the anti-knock properties of some specific types of fuel taken as a sample. Two types of fuel were chosen as reference types: one of which detonates weakly, and the other - strongly, with such a calculation that all types of fuel to be tested were between the selected standards in terms of their tendency to detonation. The value characterizing the anti-detonation qualities of the fuel was taken to be the percentage content of low-detonation fuel in the reference mixture, which is equivalent in terms of detonation resistance to the tested sample.

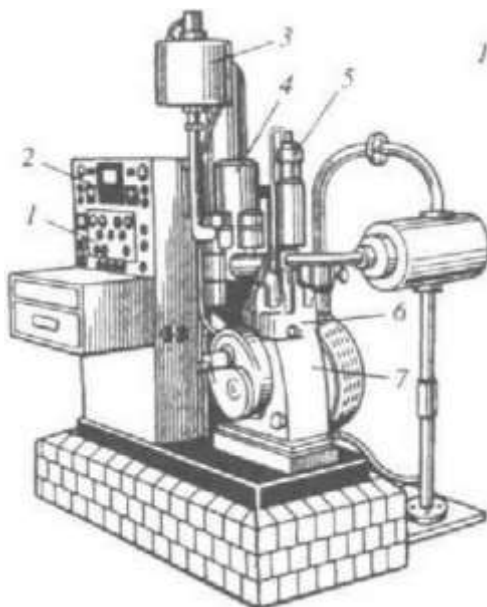
**Octane number (ON)** – is an indicator of detonation resistance of gasoline.

**To evaluate the detonation properties of gasoline**, special single-cylinder engines are used, the degree of compression of which can be changed.

The detonation resistance of gasoline is evaluated in comparison with the detonation resistance of reference fuels. Individual hydrocarbons are used as reference fuels – *isooctane* ( $C_8H_{18}$ ), the detonation resistance of which is taken as 100 units and *normal heptane* ( $C_7H_{16}$ ), the detonation resistance of which is taken as 0 units, and their mixtures.

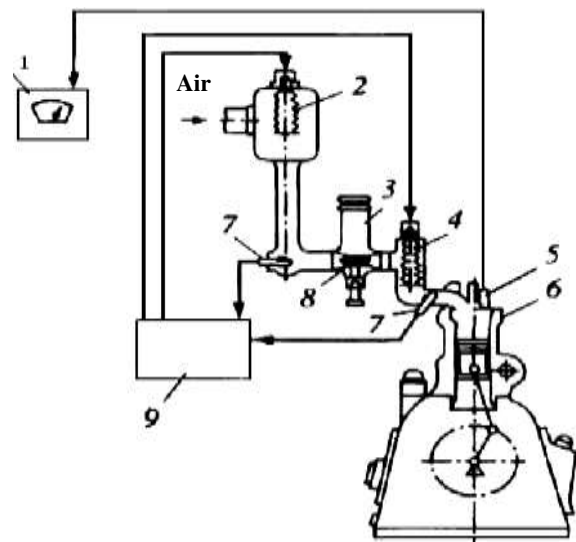
**The octane number is defined as the volume fraction (%) of isooctane in a mixture with normal heptane, equivalent in its detonation resistance to the tested fuel under standard test conditions.**

The octane number of automobile gasoline is determined by two methods – *motor and research*. The UIT-65 installation allows you to determine octane numbers by both methods. It is equipped with an electronic device for measuring the intensity of detonation and automatic devices for maintaining the necessary test mode (fig. 3.7, 3.8).



1 - electronic detonometer DP -60; 2 - VD-50 detonation indicator; 3 - air heater at the entrance; 4 - carburetor; 5 - condenser of the thermosiphon-evaporative cooling system; 6 - drive roller of the mechanism for changing the degree of compression (the handle is removed); 7 - engine crankcase.

Figure 3.7 – UIT-65 universal installation for determining the ON



1 - detonation meter; 2 - air heater; 3 - fuel tank; 4 - fuel mixture heater; 5 - detonation sensor; 6 - single-cylinder engine; 7 - temperature sensors; 8 - mixing device; 9 - device for automatic temperature regulation.

Figure 3.8 – UIT-65 installation diagram

By composing mixtures of isooctane with normal heptane in volume percentages, reference mixtures with detonation resistance from 0 to 100 units can be obtained.

Due to the difficulty of selecting a reference fuel identical to the tested one, we limited ourselves to the selection of two reference mixtures with such a calculation that the tested fuel was between them in terms of its resistance to detonation. Provided that the detonation resistance of the selected mixtures is close, the equivalent mixture can be found by calculation, based on the proportionality between the change in the octane number of the standards and the readings of the device that registers the detonation.

The use of such a technique made it necessary to measure the intensity of detonation. The main requirement for the method of assessing the intensity of detonation when comparing fuels is the ease of measurement and obtaining a reference directly during the tests. As you know, the operation of the engine with detonation is accompanied by the appearance of knocking, as well as a sharp increase in pressure at the end of combustion. These phenomena were used to measure the intensity of the detonation.

These methods (research and motor) differ in the mode of operation of a single-cylinder unit, which determines the detonation resistance of gasoline. The mode of installation, in which the octane number is determined, according to the motor method is more intense (close to the operation of trucks) than the research method (close to the operation of passenger cars). The octane number of gasoline, determined by the motor method, is lower than the octane number determined by the research method by 7-8 units.

The combustion conditions of the fuel mixture in working engines differ significantly from the mode of estimation of octane numbers of gasoline at the UIT-65 installation. Therefore, it is believed that the most objective detonation resistance is characterized by the road octane number (RON), which is determined in road conditions. In a number of cases, it differs significantly from ON, which is determined by laboratory methods – motor (ONM) and research (ONR). This is due to the design features of the engines (automotive and single-cylinder laboratory), different modes of their operation. The difference in RON, ONM and ONR (road sensitivity) can vary widely and depend on the component and hydrocarbon composition of gasoline.

RON of gasoline is determined on a specially prepared car. The organization of such tests is difficult (GOST 10373-75 strictly regulates road and meteorological test conditions), their conduct is long and possible only in the summer period. All this requires large material and labor costs. Therefore, such tests are usually carried out only when working out the design of automobile engines of new models and selecting the component composition of gasoline of new brands.

The detonation resistance of gasoline depends on the mixture the engine is running on. Isomers of paraffinic hydrocarbons are distinguished by the greatest detonation resistance when working on lean mixtures, and aromatic hydrocarbons on rich ones. The lowest detonation resistance is characteristic of normal paraffin hydrocarbons.

The middle position between them is occupied by naphthenic and unsaturated hydrocarbons.

Octane numbers of gasoline can be increased using modern technological processes; adding high-octane components, as well as introducing anti-detonation additives – **ANTI-DETONATORS**.

*The first method* – is the use of modern technologies for obtaining fuels, for example, catalytic cracking, reforming, etc. Modern technology makes it possible to obtain base

gasolines with a concentration of 75-80 according to the motor method and 80-94 according to the experimental method.

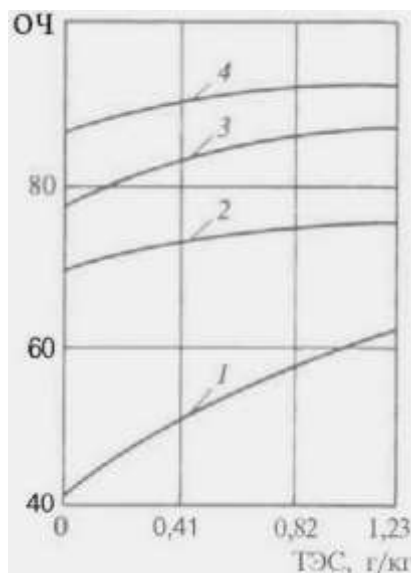
**The second way** to increase the ON is to add high-octane components to base gasoline, such as isooctane, alkylbenzene, and others, which have an ON of about 100 units according to the motor method. Such components can be added to base gasoline up to 40%, significantly increasing its detonation resistance.

**The third way** to increase the detonation resistance of gasoline is to add anti-detonation additives and octane-enhancing additives to them.

Since 1923, the problem of increasing the detonation resistance (increasing the octane number) of gasoline in most cases was solved by adding ethyl liquid (EL), which includes tetraethyl lead (TEL)  $Pb(C_2H_5)_4$ , which led to a contradiction with environmental safety the environment in some countries, tetramethyl lead  $Pb(CH_3)_4$ , which has a lower boiling temperature ( $100^\circ C$ ) compared to TEL ( $200^\circ C$ ), was also widely used. Both anti-detonators are very poisonous.

The mechanism of action of antidetonators, in particular tetraethyl lead, is most fully explained by the peroxide theory of detonation and the theory of chain reactions by N.M. Semenov It was established that TEL acts as an anti-detonator only at high temperatures, when it begins to disintegrate with the formation of atomic lead.

It is characteristic that the presence of TEL inhibits the formation of oxygen-containing compounds in gasoline. This reduces the probability of detonation. Large concentrations of TEL cause a sharp increase in the toxicity of gasoline. At the same time, the reliability of the engine is reduced due to the accumulation of lead oxides in the combustion chamber. And the detonation resistance increases slightly (fig. 3.9).



1 - direct distillation; 2 - thermal cracking; 3 - catalytic cracking; 4 - reforming.

Figure 3. 9 – The influence of TEL content on the octane number of gasoline (according to the motor method)

Previously, TEL antidetonator was used as an antidetonator, which is a heavy, oily, colorless and highly poisonous liquid that easily dissolves in all petroleum products and does not dissolve in water (density  $1652 \text{ kg/m}^3$ , boiling point  $200^\circ C$ ).

Leaded gasoline is very toxic.

Penetrating into the human blood through the pores of the skin, TEL has the property of gradually accumulating in it, which leads to difficult-to-treat, and sometimes incurable diseases. TEL also enters the body through the respiratory tract, and even minimal doses of it in food cause fatal poisoning. Working with leaded gasoline requires strict adherence to safety rules.

Leaded gasolines are a source of lead pollution of the environment and an obstacle to the use of catalytic systems for neutralization of exhaust gases on cars, because their catalytic base is quickly poisoned by lead oxides.

In Ukraine, the production of leaded gasoline is prohibited, and one of the solutions to increase the anti-knock properties of fuels and meet environmental requirements is to replace toxic anti-knock agents with much less toxic anti-knock additives, such as methyl tert-butyl ether (MTBE) -  $\text{CH}_3\text{OC}_4\text{H}_9$ .

It is non-toxic, has a higher heat of combustion, good mixing with gasoline in any ratio, and is not aggressive to structural materials. When MTBE is added to gasoline in the amount of 11%, the cold start temperature of the engine decreases by 10-12°C. When adding 10% MTBE, the octane number of gasoline increases by 2.1-5.8 units. (according to the experimental method), and with the addition of 20% - by 4.6-12.6 units.

The maximum permissible content of MTBE or Fetherol in domestic gasoline is 15%.

As anti-knock additives, the use of compositions containing manganese and iron in the form of cyclopentadienyltricarbonyl manganese (CTM) and bicyclopentadienyl iron (ferrocene) and its derivatives is envisaged. "Octane-Maximum" additive (TU 6-00-05008008-002-96) was developed on the basis of iron dicyclopentadienyl. In addition, tests were carried out on automobile gasolines containing the FK-4 (ferrocenyldimethylcarbonyl) additive. Tests have shown that the introduction of FK-4 additive provides a reduction in harmful emissions with exhaust gases (for CO by 10-20%, for hydrocarbons - by 1.2-2.4 times). The condition of the spark plugs after 4,000 km. satisfactory. No interruptions in the inflammation system were detected.

According to the results of bench and operational tests, ferrocene-based anti-detonators are approved for use when the iron content in gasoline of all brands is no more than 37 mg/dm.

Manganese anti-detonator has passed extensive tests in our country and is used in some foreign countries. MCTM is a crystalline substance with a melting point of 76°C, dissolves well in gasoline and does not dissolve in water, has high anti-knock properties. Gasolines containing CTM have good low-temperature properties, unlike TEL, they do not lead to rapid poisoning of exhaust gas neutralizers. The toxic properties of manganese and iron compounds used as additives based on them are significantly lower than TEL.

Low-toxic nitrogen-containing additives - aromatic amines - are also approved for use as anti-knock additives. Among them, the additive ADA has become widely used.

Measures to improve the environmental performance of gasoline and replace tetraethyl lead (TEL) with high-octane hydrocarbon or oxygen-containing components cannot be implemented by all oil refineries (refineries) due to various technological and financial capabilities. Therefore, other anti-knock additives or additives are being developed and tested, as it was mentioned, as substitutes for TEL. Table 3.1 lists the most common TEL substitutes and their technical indicators.

Table 3.1 – Anti-knock efficiency of various anti-knock additives and additives

Name additives or supplements	The amount of additives or supplements is increased by 1 oct. unit 1 ton of gasoline, kg	The maximum increase in the octane number at the permissible concentration of the additive in gasoline, units.
Ethyl liquid	0,07	X
Additive MCTM	0,1	5
FK-4 additive	0,07	3
Additive ADA	2,5	6
MTBE	30	4,5
Feterol with MCTM (brand D)	8	6,5
Farrad's addition	1,33	7,5

From the data presented, it can be seen that the introduction of TEL into gasoline is the most effective and cheapest way to increase the octane number of gasoline, but due to its high toxicity and incompatibility with car exhaust gas neutralizers, its use is prohibited and limited.

At present, work on the use of metal-containing anti-detonators, as already mentioned above, based on iron and manganese compounds, is quite active. According to the results of numerous tests, the possibility of their use in the composition of automobile gasoline has been confirmed. They have high anti-knock properties, as already mentioned, are less toxic compared to TEL, but they also have disadvantages.

Thus, gasolines with manganese antidetonators (CTM, MCTM) produce increased deposits on the surfaces of spark plugs and afterburner catalysts, reducing their efficiency. In addition, manganese compounds when inhaled have a neurotoxic effect, and when used in large quantities in places where cars are crowded or in closed parking lots and in repair areas, they can exceed the maximum permissible concentration.

Iron-containing additives (ferrocenes) are non-toxic, relatively cheap and effective, but cause increased wear of engine parts and varnish deposits. At low concentrations of ferrocenes (up to 40 mg/kg of gasoline), their negative impact on engine operation slows down, but does not disappear, the intensity of wear of parts decreases, but remains at a higher level than when using gasoline without additives.

Based on the ever-increasing requirements for the reliability and environmental characteristics of engines, the use of gasoline with metal-containing additives can only be considered as a temporary alternative to leaded gasoline, which does not meet the technical level of the European standard EC 228.

### 3.3 PROPERTIES OF GASOLINES AFFECTING THE FORMATION OF DEPOSITS IN THE ENGINE

**Fuel stability** – is the ability to maintain properties within acceptable limits for specific operating conditions. The stability of fuels depends primarily on their physical and chemical properties (density, viscosity, boiling point, hydrocarbon composition), the presence of various impurities, etc. In operating conditions, when the fuel is exposed to external factors such as air oxygen, unstable temperature, contamination with moisture and mechanical impurities, its fractional and chemical composition deteriorates. Conditionally,

**physical and chemical stability** of fuel are distinguished, taking into account that changes in some of its physical properties may cause changes in its chemical order and vice versa.

**Physical stability of fuels.** The physical stability of the fuel is defined as the ability to **maintain the fractional composition** (changes are caused by the loss of the lowest-boiling fractions as a result of their evaporation) and **homogeneity**. The physical stability of gasoline is assessed by saturated vapor pressure and the presence of light fractions. Insufficient physical stability in a number of cases is determined by the high volatility of gasoline.

The design of the fuel tanks should prevent free communication of their internal volume with the atmosphere. To exclude evaporation, fuel tanks are protected from direct sunlight by car design elements or special screens. This allows you to minimize their heating by the sun's rays and heat from the engine.

The physical stability of the fuel is evaluated and controlled by periodically determining the density, fractional composition, saturated vapor pressure, solidification temperature and other indicators.

The content of aromatic hydrocarbons in the fuel is allowed in limited quantities. This is due to the fact that they have the highest hygroscopicity compared to other carbons.

**Chemical stability.** The chemical stability of fuel is understood as its ability **to keep its chemical composition unchanged**.

In the conditions of long-term storage, some of the compounds (sulfur, oxygen, nitrogen, and organometallic) can undergo oxidation reactions (the main reaction that causes a change in the operational properties of hydrocarbon fuels), polymerization, and condensation.

The chemical stability of gasoline depends on the composition and structure of the hydrocarbons included in them. The most prone to oxidation are unsaturated hydrocarbons, the interaction of which with air oxygen depends on their structure, number and location of double bonds. Paraffinic, naphthenic, and aromatic hydrocarbons oxidize relatively slowly under conditions of storage and transportation. Oxygen compounds formed in the oxidation process are themselves catalysts that accelerate further fuel oxidation. Therefore, this process is evaluated as self-accelerating or automotive catalytic. Fuel oxidation increases as its temperature increases.

The process of hydrocarbon oxidation is explained by the theory of chain reactions, the course of which is accompanied by the formation of unstable intermediate compounds - peroxides, which decompose along with the final products, releasing an amount of energy sufficient to continue the reaction chain without supplying energy from the outside.

The content of acids and other products with an acidic reaction in the fuel is characterized by an indicator called fuel acidity, with an increase in which its corrosive aggressiveness increases and engine wear increases. Its value is determined by the amount of KOH alkali in mg, which is needed to neutralize 100 ml of fuel.

The presence of sulfur compounds (especially disulfides and mercaptans) in the fuel worsens its stability and contributes to tar formation.

As a result of gasoline oxidation, soluble organic acids and resinous substances are formed. The content of actual resins - the products of oxidation, polymerization and condensation reactions determine the degree of gasoline tarification.

The content of actual resins, standardized by standards, is determined by hot air evaporation of a certain amount of fuel at an elevated temperature (for gasoline 150°C,

diesel fuel 250°C) based on the residue obtained after evaporation. The presence of actual resins is estimated in milligrams per 100 ml of fuel. For gasoline, for example, it is no more than 5 mg/100 cm<sup>3</sup> at the place of production, and at the place of consumption 10 mg/100 cm<sup>3</sup> according to GOST 2084-77, and according to GOST 51105-97 one value is entered - at the place of consumption - no more than 5 mg/100 cm<sup>3</sup>.

Since the hydrocarbons that make up the fuel are colorless, its yellow-brown coloring is due to the presence of resinous substances in it. Therefore, the presence of resins in the fuel can be visually judged by its color.

With the content of actual resins within the limits allowed by the standards, the engines work for a long time without increased resin and soot formation. If the content of resins is two to three times higher than the norm, which is a common phenomenon during the operation of cars, then the engine life of a gasoline engine is reduced by 20-25%, and, in addition, various problems occur (valves hang, etc.).

The ability of gasoline to keep its composition unchanged under the conditions of transportation, storage and use is assessed by the *induction period (evaporation index)*. This indicator is determined by the time in minutes from the beginning of gasoline oxidation to the active absorption of oxygen by it in a laboratory installation (hermetic vessel) during the artificial oxidation of gasoline (temperature 100±1 °C in an atmosphere of dry and pure oxygen at a pressure of 0.7 MPa). This time for gasoline of different brands ranges from 360 to 1250 minutes. Gasoline used in winter should have a high volatility index. Significant accumulation of resins and other oxidation products, unacceptable deterioration of the operational properties of gasoline begins after the oxidation time exceeds the induction period.

The low chemical stability of fuels affects the formation of various deposits on engine parts, which leads to deterioration of its operation.

To increase the chemical stability of gasoline distillates, hydrotreating is the most promising. This method makes it possible to increase stability and reduce the content of sulfur compounds.

It is believed that the most effective and economically beneficial way to increase the chemical stability of gasoline fractions is the introduction of special multifunctional antioxidant additives - compounds of phenolic, amine, and aminophenolic types, capable of interrupting oxidation chain reactions, inhibiting oxidation processes in gasoline, thereby increasing the induction period of oxidation. In addition, such additives provide fuels with anti-wear (lubricating) and protective (anti-corrosion) properties. Gasoline is stabilized with the following antioxidants: wood-resin, FC-16, p-oxydiphenylamine, ionol.

***Pollution of gasoline.*** According to the standards, gasoline should not contain mechanical impurities - solid particles of organic and inorganic origin that remain on the paper filter after filtering a certain amount of fuel.

It has been established that mechanical impurities (soil dust, corrosion products of factory equipment, tanks, pipelines, wear products of pumping equipment, etc.), entering the combustion chambers of engines, cause increased wear of piston rings and cylinder walls. Therefore, increasing the purity of gasoline is an important factor in increasing the reliability and durability of the engine.

### 3.4 CORROSION PROPERTIES OF GASOLINES

*Minimal corrosive effect* on metals is one of the main requirements for gasoline. **Corrosion** – is the spontaneous destruction of solid bodies caused by chemical and electrical processes that develop on the body's surface during its interaction with the external environment.

Fuel can cause metal corrosion both in liquid and gaseous state.

Tanks, cisterns, fuel tanks, pipelines, parts of fuel equipment are subject to corrosion. This is facilitated by the presence of corrosive-aggressive compounds in the fuel: water-soluble (mineral) acids and alkalis, active sulfur compounds, water, organic acids.

**Water-soluble acids and alkalis** in gasoline must be absent. However, water-soluble acids and alkalis can enter the fuel during transport and storage, for example, when containers are not cleaned properly. In such cases, the presence of sulfuric acid, caustic soda, sulfonic acids and other substances that cause strong corrosion of non-ferrous and ferrous metals is not excluded.

The basis of acidic organic compounds, which are almost always contained in fuel, are naphthenic acids R-COOH and phenols (more often C<sub>6</sub>H<sub>5</sub>OH). They are most active in relation to non-ferrous metals (lead, zinc), and their activity increases with increasing temperature, and decreases with increasing molecular weight. The content of organic acids in fuels is characterized by acidity - it is normalized by the amount of alkali (in milligrams) required to neutralize the acids contained in 100 ml of fuel.

**Sulfur compounds** are divided into active and inactive according to their corrosiveness. Their content in the fuel has a negative effect on its operational properties, such as stability, ability to form soot, corrosion aggressiveness, other. **Active sulfur compounds** cause corrosion of metals even under normal conditions, their presence in fuel *is unacceptable*.

**Inactive sulfur compounds** are not dangerous for reservoirs, pipelines, fuel tanks and other parts of cars, since the corrosion process does not occur when in contact with metals.

During combustion, both active and inactive compounds form sulfuric and sulfurous anhydrides SO<sub>2</sub> and SO<sub>3</sub> (water is formed from combustion products during condensation). When combined with water, they form sulfuric and sulfurous acids. Sulfuric anhydride when the engine is hot causes gas corrosion of the cylinder, piston and exhaust valves. According to the results of numerous experiments and practical data, it was established that corrosive wear largely depends on engine wear, the amount of sulfur contained in the fuel, and specific operating conditions: when the sulfur content in gasoline increases from 0.05 to 0.1%, engine wear increases 1.5-2 times, from 0.1 to 0.2% - another 1.5-2 times, and from 0.2 to 0.3% - 1.3-1.7 times.

### 3.5 ENVIRONMENTAL REQUIREMENTS FOR GASOLINES

Environmental issues in the modern world have acquired a worldview and moral character. This is due to the objective reality of the global ecological crisis, the negative impact of the technosphere on the biosphere.

It is known that 90% of the harmful substances entering the atmosphere of our cities come from road transport.

**Combustion products of motor fuels are one of the main pollutants of the air pool.** As the volume of fuel consumption increases, the content of toxic components of engine exhaust gases in the air increases.

Gasoline vapors also pose a great threat to human health, the content of which in the atmosphere increases with the increase in the production of petroleum products. As a result, improving the quality of gasoline, in order to increase the environmental safety of their use, can be achieved by changing the hydrocarbon and chemical composition of fuels. Reference points in the development and implementation of gasoline with improved environmental performance are the norms of the European standards for gasoline EK 228, as well as the actual quality indicators of European fuels, which, as a rule, are higher than the norms regulated by international standards.

The problem of improving the quality of gasoline is solved by:

- refusal to use lead compounds in gasoline;
- reduction of sulfur content in gasoline to 0.05%, and in the future to 0.003%;
- reducing the content of aromatic hydrocarbons to 45%, and in the future to 35%;
- standardization of the concentration of actual resins in gasoline at the point of use at a level of no more than 5 mg per 100 cm<sup>3</sup>;
- differentiation of quality indicators by fractional composition and pressure of saturated steam (8 classes) taking into account the season of operation of automotive equipment and the temperature background characteristic of a specific climatic zone. The presence of 8 classes allows us to offer the consumer gasoline with optimal properties depending on the actual ambient air temperature, which ensures the operation of engines without the formation of vapor jams at air temperatures up to plus 60°C and guarantees high evaporation of gasoline and easy engine start at temperatures below minus 35 °C;
- introduction of cleaning additives that prevent contamination and tarnishing of fuel equipment parts.

Studies of the environmental efficiency of the use of gasoline have shown that:

- if the quality of gasoline is improved to the level of the European standard in terms of sulfur, benzene content and in the absence of lead, the environmental aggressiveness of exhaust gases decreases by 4%;
- when using MTBE, the aggressiveness of exhaust gases decreases by 3%, mainly due to the replacement of aromatic components of gasoline with an oxygen-containing additive and more complete combustion of fuel (reduction of CO by 12%);
- the introduction of a detergent additive helps to reduce aggressiveness and emissions by 5%.

### 3.7 CONTROL QUESTIONS

1. What kind of fuel combustion is called detonation and how does it affect the operation of the engine?
2. What is laryngeal inflammation and what damage does it cause to the engine?
3. What methods are used to prevent detonation combustion in the engine?
4. How is the detonation resistance of gasoline evaluated?
5. What compounds are used as anti-knock additives?
6. What does fuel stability depend on?
7. By what indicators is fuel stability assessed and by what means is it increased?
8. What compounds found in gasoline cause its corrosion aggressiveness and how can it be prevented?
9. What affects the environmental safety of gasoline?
10. What brands of gasoline are used in road transport?

## LECTURE 4. DIESEL FUEL (part 1)

Lecture plan:

- 4.1 Operational requirements.
- 4.2 Mixture formation.
- 4.3 Self-ignition and cetane number. Flash temperature.
- 4.4 Evaporation. Tendency to soot formation.
- 4.5 Control questions.

### 4.1 OPERATIONAL REQUIREMENTS

The main advantage of diesel engines is their high efficiency. They consume 25...30% less fuel compared to gasoline engines. Economic operation of diesel engines is achieved mainly due to high compression ratios. In high-speed diesel engines, it reaches 18. Diesel fuel is cheaper than gasoline, since it is mainly obtained by direct distillation.

Diesel engines are more reliable and durable. They are characterized by stable efficiency in the entire range of loads, better acceptance and the ability to work with the load without full warm-up. The main differences in the operation of diesel and gasoline engines are the methods of mixture formation and ignition of the working mixture. Therefore, the requirements for diesel fuel are determined by the features of the engine.

Diesel fuel must have good atomization, mixture formation, evaporation and pumping, quick self-ignition; to burn completely, and without smoking; not to cause increased soot and varnish formation on valves and pistons, coking of the nozzle atomizer, freezing of the atomizer needle, corrosion of tanks, tanks, engine parts, etc.

The main operational indicators of diesel fuel:

- cetane number, which determines the power and economical performance of the engine;
- low-temperature properties that determine the operation of the power supply system at negative ambient temperatures;
- viscosity and density, which ensure normal supply of fuel, its atomization in the combustion chamber and the efficiency of fuel filters;
- fractional composition, which affects the completeness of combustion, smoke and toxicity of exhaust gases;
- degree of cleanliness, which determines the reliability of coarse and fine filters;
- flash point, which characterizes the safety conditions of fuel use in engines;
- corrosive properties caused by the presence of sulfur compounds, unsaturated hydrocarbons, water-soluble acids and alkalis.

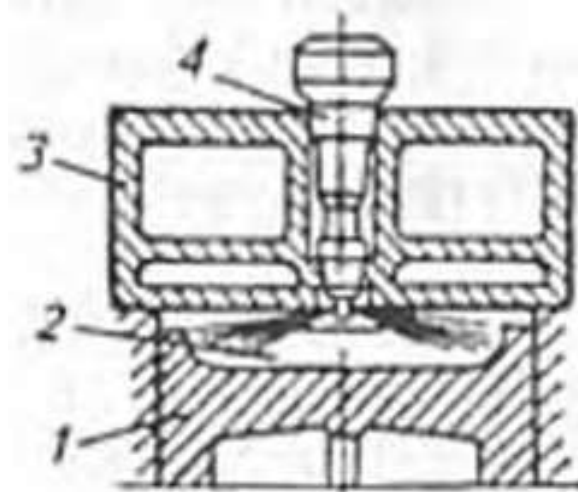
### 4.2 MIXTURE FORMATION

The process of mixture formation in a diesel engine is a complex complex of physical and chemical phenomena that occurs from the moment of fuel injection into the combustion chamber until the ignition of its portion.

Diesels belong to engines with internal mixture formation. Fuel is injected into the cylinder through the nozzle at the end of the compression stroke. In this, the speed of the fuel jet reaches 150...400 m/s. The air pressure in the cylinder is more than 2.9 MPa at a normal temperature of about 600°C. The friction of the air and the jet of fuel causes its

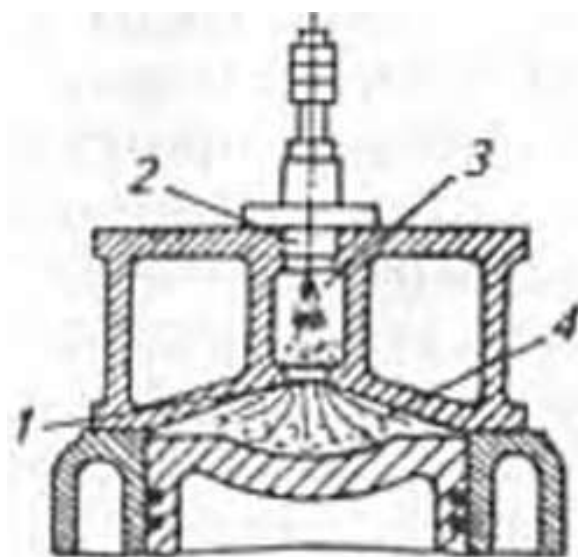
destruction into droplets with a diameter of 2...3 microns. Fuel atomization and the nature of air movement in the cylinder depend on the design of the combustion chamber.

Combustion chambers of diesel engines are undivided and divided. In undivided combustion chambers (fig. 4.1), the entire compression space is a single volume into which fuel is directly injected. Since the mixing process takes place in a single volume, very high requirements are placed on the quality of spraying.



*1 - piston; 2 - combustion chamber; 3 - cylinder head; 4 - nozzle.*  
Figure 4.1 – Diagram of a non-divided combustion chamber

Pre-chamber diesels have a split combustion chamber. Such a combustion chamber consists of the main chamber 4 (fig. 4.2) and the pre-chamber 3. Fuel burns in the chamber partly due to lack of air. The rest of the fuel, due to a sharp increase in pressure during combustion, is ejected at high speed through the connecting channels into the main chamber. At the same time, the main part of the fuel is also sprayed, mixes with the air that is in the main chamber, and burns out.



*1 - connecting channel; 2 - nozzle; 3 - prechamber;  
4 - the main combustion chamber.*  
Figure 4.2 – Schematic of a split combustion chamber  
of a pre-chamber diesel engine

Along with the design of the combustion chamber, the quality of the mixture is influenced by fuel properties: density, viscosity, saturated vapor pressure, surface tension, fractional composition.

An increase in **fuel density** affects the process of mixture formation in the same way as an increase in viscosity: the length of the jet increases, engine efficiency deteriorates, and smoke increases. At low fuel density, the length of the jet decreases, the process of mixture formation deteriorates. Therefore, the density of diesel fuel should be optimal, taking into account the seasonality of operation and other factors, and be within the range of 830...860 kg/m<sup>3</sup>.

**The viscosity** of diesel fuel affects the quality of fuel atomization and mixture formation, pumping, operation of the fuel pump, wear of precision pairs of the high-pressure pump, for which the fuel simultaneously serves as a lubricant, completeness of combustion and fuel consumption, composition of exhaust gases. Due to high viscosity, interruptions in the supply of fuel to the pump may occur due to high resistance when it flows through the fuel system. The lower the viscosity, the finer the atomization of the fuel, the smaller the diameter of the droplets formed, the better the evaporation. However, at the same time, the length of the fuel jet decreases (since small droplets have low kinetic energy), uneven formation of the combustible mixture, incomplete combustion and excessive fuel consumption are observed.

As the viscosity increases, the length of the jet increases. At the same time, part of the drops falls on the walls of the combustion chamber, as a result of which the process of mixture formation, evaporation, and completeness of fuel combustion deteriorates. This leads to excessive consumption of fuel, a decrease in power, and an increase in smoke of exhaust gases. For summer types of fuel, the viscosity should be 3...6 sSt, for winter - 1.8...6 sSt.

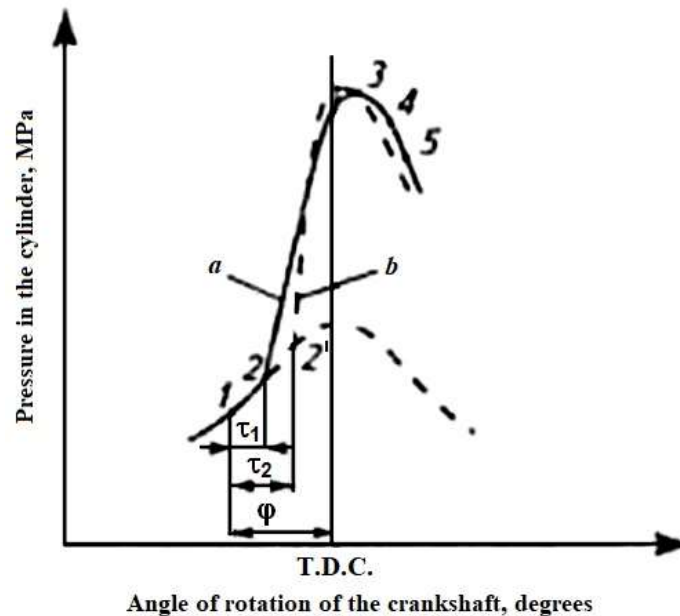
#### **4.3 SELF-IGNITION AND CETANE NUMBER. FLASH TEMPERATURE**

**Self-ignition.** The working process of a diesel engine differs from the process of a gasoline engine in the preparation and ignition of the combustible mixture. Ignition of the combustible mixture in diesel engines occurs without an external ignition source. The mixture self-ignites under the influence of high temperature as a result of oxidation reactions rapidly occurring in it figure 4.3 shows the indicator diagram of a diesel engine, i.e. the diagram of the pressure change in the middle of the cylinder depending on the angle of rotation of the crankshaft.

The supply of fuel by the nozzle into the combustion chamber begins at point 1 after 10...20° of the crankshaft rotation angle to the t.d.c. Fuel injection ends in different engines in different ways: as after t.d.c. and to her. ***The angle between the beginning of the fuel supply and the t.d.c. is called the fuel injection advance angle and is denoted  $\varphi$ .*** The duration of fuel injection corresponds to the period from the beginning to the end of fuel supply.

Ignition of the combustible mixture occurs some time after fuel is injected into the combustion chamber. This time is called ***the self-ignition delay period***. Self-ignition of fuel vapors (at point 2) is preceded by a certain period during which a number of physical and chemical processes take place. The fuel is sprayed in hot air, its droplets are heated to a high temperature and evaporate.

Under the influence of high temperature and oxygen, pre-flame reactions of multistage oxidation of hydrocarbons, which are part of the fuel, occur. Oxygen-containing compounds accumulate in the working mixture, which then begin to decompose with the release of part of the heat (10...15%) and oxygen. Cold-flame oxidation leads to an increase in the temperature of the mixture and the appearance of many ignition foci. At this moment, a blue glow appears, which is called a "cold" flame. As a result of an increase in the temperature of the mixture, the rate of chemical reactions increases, its ignition occurs, that is, the appearance of a hot flame.



*a - during normal operation; b - during hard work;  
 1 - start of injection; 2 - self-ignition of fuel; 3 - the end of rapid combustion;  
 4 - the end of slow combustion; 5 - the end of afterburning.*

Figure 4.3 – Expanded diesel indicator diagram

Fuel combustion begins at point 2. Most of the fuel has managed to evaporate by this point, and the combustion process includes new portions of the combustible mixture. The fuel continues to be supplied by the nozzle into the combustion chamber, it intensively combines with air, evaporates and burns quickly. Due to the rapid combustion of fuel, the pressure in the cylinder increases significantly. The period of rapid combustion continues from point 2 to point 3. In this period, the main amount of thermal energy of the cyclic fuel supply is released (up to 70%), the fuel supply by the injector continues, and the pressure increases. The end of the period is conditionally considered to be point 3, at which the maximum pressure is reached. At the end of rapid combustion, the increase in pressure stops, the combustion rate decreases.

After point 3, the period of slow combustion begins, the pressure increases slightly. The fuel supply stops, but the combustion process continues and the temperature of the gases rises. About 20% of the thermal energy of the fuel is released. The decrease in pressure at the end of the period (point 4) is explained by the increase in the volume of the combustion chamber and the connection with the movement of the piston to b.d.c. At the end of the delayed combustion period, point 4 is conditionally accepted, when the maximum temperature of the combustion chamber gases is reached. Then there is the

afterburning of fuel residues and incomplete combustion products. ***The heavier the fuel, the higher its viscosity and density, the longer the afterburn period.*** The afterburning phase can reach 70° of the crankshaft rotation angle to top dead center.

With a long period of delay of self-ignition of the combustible mixture in the diesel cylinder, most of the fuel accumulates and burns. This causes a sharp increase in pressure for each degree of rotation of the crankshaft, as a result of which the so-called hard operation of the engine is observed. The external signs of hard operation of the engine are identical to detonation combustion of gasoline in gasoline engines. If the pressure in the combustion chamber increases by 0.25...0.5 MPa at 1° rotation of the crankshaft, then the engine works normally, by 0.5...0.9 MPa – hard, and above 0.9 MPa – very hard.

The hard operation of the engine is shown in Figure 3 (curve b). At point 2', self-ignition occurs, after which the pressure increases at a high rate. When the diesel engine is working hard, the load on the parts of the crank mechanism increases, which causes their intense wear.

***The chemical composition*** of the fuel significantly affects the auto-ignition delay period. Paraffin hydrocarbons have the lowest auto-ignition temperature. The higher their molecular weight, the lower the auto-ignition temperature.

***Cetane number.*** The cetane number, which is determined according to DSTU at special installations, serves as an estimate of the self-ignition of diesel fuels. The installations have a single-cylinder four-stroke diesel with a variable compression ratio from 7 to 23. When conducting tests, the advance angle of fuel injection should be 13° to t.d.c., and the injection pressure should be 10.4 MPa.

Paraffin hydrocarbon cetane and aromatic hydrocarbon alphas-methylnaphthalene were chosen as reference fuels. Cetane has a very short autoignition delay period, and its cetane number is conventionally taken as 100. Alphas-methylnaphthalene has a long autoignition delay period, and its cetane number is conventionally taken as 0. Mixtures of cetane and alphas-methylnaphthalene in different ratios have different autoignition.

The cetane number of diesel fuel is determined as follows. Start the engine on the tested fuel and, by changing the compression ratio, ensure that the self-ignition of the fuel begins exactly at the t.d.c. Then a mixture of cetane and alphas-methylnaphthalene is selected, which, at the same compression ratio, also ignites in the t.d.c., has the same autoignition delay period as the tested fuel.

***The cetane number – is the percentage (by volume) content of cetane in a mixture with alphas-methylnaphthalene, which is similar to the tested fuel in terms of autoignition.*** For example, if the tested diesel fuel has a cetane number of 47, it is equivalent to an artificial mixture of reference fuels containing 47% cetane and 53% alpha-methylnaphthalene in terms of self-ignitability.

The cetane number of diesel fuel depends on its chemical composition and tendency to oxidation. Paraffinic hydrocarbons of normal structure oxidize and disintegrate the fastest. They have the highest cetane numbers. Aromatic hydrocarbons are self-igniting at higher temperatures and over a longer period of time and have the lowest cetane numbers.

Various additives can be used to increase the cetane number of diesel fuels, such as isopropyl nitrate or cyclohexyl nitrate. However, the production of these additives has recently been discontinued. Specialists of the company "Unicol" have developed a new effective additive "Miakron-2000", the basis of which is ethylhexyl nitrate. The mass fraction of the additive in diesel fuel should be 0.1...0.3%.

Additives accelerate the initial pre-flame reactions and contribute to the formation of new active reaction centers. ***The lower the cetane number, the higher the stiffness of the diesel engine.*** Other indicators of engine performance depend on the value of the cetane number: its start, average effective combustion pressure, specific fuel consumption, temperature of exhaust gases, deposits in the engine, smoke and smell of exhaust gases. With an increase in the cetane number of the fuel, it becomes easier to start the engine and the average combustion pressure increases, other indicators decrease, the operation of the engine generally improves.

For modern tractor-trailer diesel engines, fuel with a cetane number of at least 45 is used. With a cetane number of diesel fuel of 40 and below, diesel engines work hard. However, increasing fuel cetane numbers above 51 does not cause a significant improvement in diesel performance, and specific fuel consumption and smokiness increase due to a decrease in completeness of combustion.

The cetane number (CN) of diesel fuel is calculated according to various formulas, the main of which are the following:

at a known density  $d_4^{20}$  and kinematic viscosity  $\nu_{20}$

$$CN = (\nu_{20} + 17,8) \cdot \frac{1,5879}{d_4^{20}};$$

with a known hydrocarbon composition

$$CN = 0,85P + 0,1N - 0,2A,$$

where P, N, A – are the content of paraffinic, naphthenic, and aromatic hydrocarbons, respectively.

***Flash temperature.*** This parameter is used to assess the quality of fuel and to classify production, premises and installations according to the degree of fire danger.

The flash temperature – is the minimum temperature at which fuel vapors, heated in a special apparatus, form a combustible mixture that ignites when a flame is raised to it. The flash temperature characterizes the danger of diesel fuel during its transportation, storage and refueling.

#### **4.4 EVAPORATION. TENDENCIES TO BURNING**

***Evaporation.*** To obtain a high-quality combustible mixture, the fuel must evaporate completely in the combustion chamber. The completeness of its combustion, starting and operation of the engine, soot and varnish formation, wear of engine parts and its efficiency, the composition of exhaust gases, and oil consumption depend on the evaporation rate of the fuel. The volatility of diesel fuel is estimated by fractional composition, distillation temperatures of 50 and 90% or 50 and 96% of the fuel.

Fractional composition has a greater influence on engine start than cetane number. When starting the engine, the least favorable conditions for mixture formation and fuel combustion are created due to insufficiently high temperature in the combustion chamber. ***The more light fractions in the fuel, the faster and more completely they evaporate.*** In

light fuel, the diameter of the droplets formed is smaller, and their evaporation area is larger. The starting properties of diesel fuels are characterized by ***the boiling point of the 50% fraction. The lower this temperature, the easier it is to start the engine***, especially at low ambient temperatures. However, lightening the fractional composition leads to an increase in the auto-ignition delay period.

Fuels of heavy fraction composition with a high boiling point of 96% of the fraction do not have time to completely evaporate, and therefore burn. Incomplete combustion leads to excessive consumption of fuel, increased smokiness of exhaust gases, reduced power, increased varnish formation and soot formation. Part of the fuel in liquid form flows down the walls of the cylinder into the oil sump, washing away the lubricant and increasing the wear of engine parts. Economy and durability of the engine deteriorate. Therefore, excessive weighting of fuel, as well as its lightening, are undesirable.

***Tendency to soot formation.*** One of the important operational properties of diesel fuel is the ability to ensure the cleanliness of the engine and fuel equipment. This property depends on the chemical and fractional composition of the fuel. During fuel combustion, soot formation is observed on the walls of the combustion chamber and intake valves, as well as on the nozzles and needles of the nozzles. On the walls of the combustion chamber, the bottoms of the pistons and the intake valves, a dense, hard soot of a dark color forms, and on the nozzles and needles of the nozzles, a soft, resinous soot of a yellowish color, sometimes in the form of a light brown varnish film.

Deposit of soot on the walls of the combustion chamber worsens the removal of heat to the engine cooling system. The presence of soot on the intake valves leads to coking, as a result of which the correct fit of the valve plate on the seat is disturbed. There is a leak of hot gases and burning of the seating surfaces of the valve and the seat, and in some cases the valve hangs.

The biggest malfunctions in the operation of diesel engines are associated with soot deposits on the nozzles. Due to soot on the atomizers, the quality of fuel atomization deteriorates and the spray torch is distorted. When fuel atomization deteriorates, mixture formation is disturbed, its combustion is incomplete, which leads to smoke, a decrease in diesel power, and increased fuel consumption.

Falling of resinous deposits on the needles of sprayers contributes to their freezing. Coking of nozzles and sticking of sprayer needles are accompanied by fuel leakage, since in this case the needle does not sit on the compacted cone of the sprayer and does not block its channel. When fuel leaks, there is also a decrease in the power and efficiency of the diesel engine, as well as its smoke.

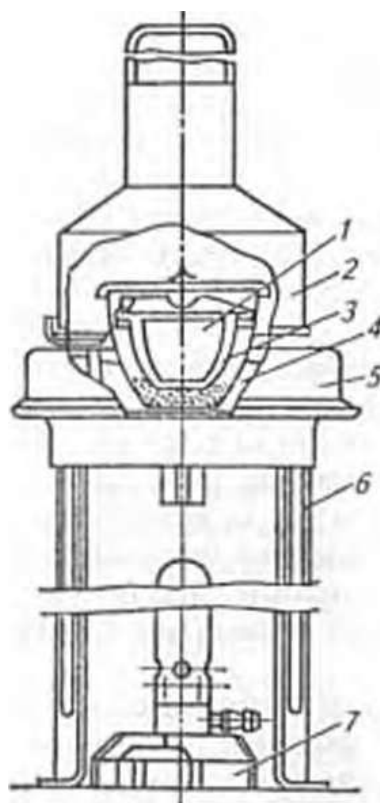
***Soot formation*** in the engine depends on the following parameters of diesel fuel: actual tar and sulfur content, fractional composition, amount of unsaturated and aromatic hydrocarbons, ash content and coking. With an increase in the content of actual resins in the fuel, soot formation on engine parts, coking of nozzle holes and sticking of needles increases. An increase in the sulfur content in fuel leads to an increase in soot and varnish, and the density of soot increases significantly.

As the ash and coking content of diesel fuel increases, its tendency to soot formation increases. Ashiness characterizes the content of non-combustible impurities in the fuel, which fall into soot, increasing its abrasive properties.

***Coking*** – is the property of fuel to form sediment (coke) when heated without access to air. Coking is determined for 10% of the residue after the preliminary distillation

of diesel fuel. Coking of 10% of the remaining fuel depends on its fractional composition and the content of tar-asphalt compounds. For diesel fuel of various brands, coking is within 0.2...0.3%.

Coking of diesel fuel is determined by the Conradson method in a special apparatus with porcelain 1 (fig. 4.4), internal 3 and external 4 crucibles. A muffle 5 is installed on the tripod 6 of the apparatus, which is heated by a gas burner 7. The crucibles and lids of the apparatus are made of sheet corrosion-resistant and heat-resistant steel.



*1 - porcelain low crucible; 2 - cap;  
3, 4 - internal and external crucible; 5 - muffle;  
6 - tripod; 7 - gas burner.*

Figure 4.4 – Conradson's apparatus for determining the coking of petroleum products

10% of the remaining diesel fuel is obtained on the device for dispersing petroleum products. Then the overhang of the residue is brought into a porcelain crucible, which is installed in the inner crucible. The inner crucible is placed in the outer one, on the bottom of which sand is poured. Both crucibles are closed with lids and a cap, which ensures uniform heating. A gas burner is installed under the bottom of the outer crucible. The flame of which should be high and not smoke. When smoke appears above the upper cylinder of the cap, fuel vapors are ignited. The flame of the burner is significantly reduced. The burning period is considered complete if there is no blue smoke above the cap.

After burning, the flame of the gas burner is increased and the lower part of the outer crucible is heated to a red temper. Roast the outer crucible. Then the burner is removed, the cap and lid of the outer crucible are removed, the porcelain crucible is removed and it is placed in a desiccator. After cooling, it is weighed.

Coking  $x$  (%) of 10% of diesel fuel residue is determined by the formula:

$$x = \frac{100m}{m_1},$$

where  $m$ ,  $m_1$  – are the mass of coke and 10% residues, respectively, g.

#### **4.5 CONTROL QUESTIONS**

1. What are the operating requirements for diesel fuel?
2. What types of mixture formation exist?
3. Good mixture formation depends on what fuel properties?
4. What is self-ignition of a mixture?
5. What is the cetane number of diesel fuel?
6. Tell about the effect of diesel fuel evaporation on engine operation.
7. What is mowing?

## LECTURE 5. DIESEL FUELS (part 2)

Lecture plan:

- 5.1 Corrosion properties.
- 5.2 Low-temperature properties.
- 5.3 Water and mechanical impurities.
- 5.4 Toxicity of diesel engine exhaust gases.
- 5.5 Assortment of diesel fuels.
- 5.6 Control questions.

### 5.1 CORROSION PROPERTIES

The cause of increased corrosion and wear of engine parts is the presence of sulfur compounds, organic acids, water-soluble acids and alkalis in the fuel. The content of organic acids in diesel fuel characterizes *the acidity of the fuel*, which should be no more than *5 mg of KOH in 100 cm<sup>3</sup>* of fuel.

*An increase in the acidity of fuels leads to an increase in corrosive wear of the plunger pairs of the high-pressure fuel pump and the growth of deposits.*

The corrosiveness of diesel fuels is significantly affected by sulfur compounds. It has been established that the general wear and tear of engine parts is approximately directly proportional to the sulfur content of diesel fuel. When the temperature of the coolant in the engine is below 70°C, the degree of corrosion wear increases, as the formation of sulfuric acid increases. Fuel combustion products containing sulfurous and sulfuric anhydrides penetrate through leaks in the cylinder-piston group into the crankcase, where they form sulfuric and sulfurous acids with water. Mixing with oil, acids deteriorate its quality, in particular anti-corrosion properties, cause rapid aging. Bearing liners, crankshaft journals and other parts are subject to chemical wear. Inserts made of lead bronze are especially prone to strong corrosion.

As a result of the action of sulfur products on the oil, tarry compounds are released, which then form soot. In the presence of sulfur compounds, soot and varnish formation in the cylinder-piston group increases. Due to the sulfur content, soot becomes hard, which leads to abrasive wear of the cylinder-piston group. The deposit of varnish in the area of the piston rings leads to their coking and jamming. Sulfuric compounds in fuel also contribute to the increase of deposits on fine and coarse oil filters.

*The lubricating capacity* of diesel fuels determines the service life of the plunger pair of the high-pressure pump. In deeply refined diesel fuels with a low sulfur content, the lubricity is significantly reduced. In this case, an additive to the fuel of anti-wear additives is required.

*The corrosion aggressiveness* of diesel fuels depends mainly on the mercaptan sulfur content. Its mass fraction in fuel is allowed no more than 0.01%. The total mass fraction of sulfur in commercial diesel fuels is 0.2...0.5%. To improve the ecology of large settlements in our country, it is planned to reduce the mass fraction of sulfur (up to 0.05...0.1%) and aromatic hydrocarbons (up to 10...20%) in fuels. Prospective quality indicators of diesel fuel abroad are as follows: in the USA – sulfur content no more than 0.003%, aromatic hydrocarbons no more than 2%; in Europe – no more than 0.005 and 3%, respectively.

Water-soluble acids and alkalis may remain in diesel fuel after treatment with sulfuric acid or alkali at the refinery. Water-soluble acids cause corrosion of all metals, and water-soluble alkalies – aluminum, so the presence of even traces of these compounds in fuel is unacceptable.

## 5.2 LOW TEMPERATURE PROPERTIES

The main operational characteristics of diesel fuel - its low-temperature properties and mobility at negative temperatures determine the operation of the power system. Fuels with a large amount of paraffinic hydrocarbons have poor low-temperature properties due to the crystallization of these hydrocarbons even at positive temperatures. The resulting crystals can clog the engine power system, especially fuel filters.

Low-temperature properties are characterized by the cloud point, the limiting temperature of filtration and the solidification temperature. *The clouding temperature* is the temperature at which the phase composition of the fuel changes, as a solid appears along with the liquid phase. At the same time, the fuel loses its transparency, becomes cloudy due to the release of microscopic ice crystals (if there is water in the fuel) and mostly solid hydrocarbons. *However, with clouding, the fluidity of the fuel does not change.* The crystal sizes are such that they pass through the filters. At the limit temperature of filtration, the size of solid hydrocarbon crystals increases and they do not pass through the filters, that is, the fluidity of the fuel deteriorates. At the solidification temperature, the crystal lattice is so strengthened that the fuel loses its fluidity.

The clouding temperature and limit temperature of fuel filtration characterize the conditions of its use. For most diesel fuels, the difference in clouding and solidification temperatures is 5...7°C. If the fuel does not contain depressant additives, then the limit temperature of filtration is equal to the clouding temperature or lower than it by 1...2°C. The air temperature at which diesel fuel can be used should be 5...10°C higher than the clouding temperature to prevent disruption of the fuel supply to the engine.

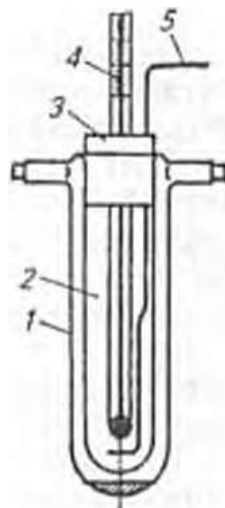
Low-temperature properties can be improved by removing part of the paraffinic hydrocarbons from the fuel, that is, *by deparaffinization*. At the same time, it is possible to obtain fuel with a predetermined solidification temperature. However, it should be remembered that high-cetane components - paraffin hydrocarbons - are removed with deparaffinization, that is, the cetane number of diesel fuel decreases. Fuels with poor low-temperature properties have high cetane numbers, while fuels with good low-temperature properties have unsatisfactory cetane numbers. To maintain the cetane number at the required level, shallow deparaffinization is carried out.

In order to ensure the required clouding and solidification temperatures, winter types of fuel are obtained by lightening the fractional composition. In the production of winter varieties of diesel fuel, *depressant additives* are used. By adding these additives in hundredths of a percent, it is possible to lower the maximum solidification temperature by 15...20 °C. In case of introduction of depressant additives, the clouding temperature of the fuel does not change. The mechanism of action of depressant additives consists in modifying the structure of crystallized paraffins, reducing their size. The low-temperature properties of diesel fuels with depressant additives are evaluated by the clouding temperature and the limiting temperature of filtration, and the fuel without a depressant – by the clouding and solidification temperature.

In order to reduce the solidification temperature of diesel fuels under operating conditions, it is allowed to add kerosene as an exception. For this purpose, low-solidifying types of kerosene (type of jet fuel) are used in the amount of up to 25%. When diesel fuel is heavily diluted with kerosene, the cetane number decreases, which leads to the engine working hard and the lubricating properties deteriorate sharply, which increases the wear of the plunger pair. At an air temperature of -20 to -30°C, the engines operate on a mixture consisting of 90% diesel fuel and 10% kerosene, and at a temperature of -30 to -35°C they operate on a mixture consisting of 75% diesel fuel and 25% kerosene. Ordinary lighting kerosene is unsuitable for this purpose, as it has poor low-temperature properties. The clouding temperature of illuminating kerosene is -12...-15°C.

The temperatures of cloudiness, onset of crystallization and crystallization are defined in DSTU 7688:2015.

The device for determining the solidification temperature of diesel fuel is shown in figure 5.1.



*1 - test tube-coupler; 2 - test tube; 3 - stopper; 4 - thermometer; 5 - stirrer.*

Figure 5.1 – Device for determining the solidification temperature of diesel fuel

The studied fuel is poured into a test tube 2 and placed in a glass test tube-coupling 1. The test tube-coupling is closed from above with a plug 3, into which a thermometer 4 is inserted. The device is placed in a vessel with a cooling mixture.

The following cooling mixtures are used:

- to obtain temperatures from 0 to -20°C - a layer of table salt and a layer of snow or crushed ice up to 3 cm are poured into the vessel alternately. Two parts of snow or ice are taken for one part of salt;

- to obtain temperatures below -20°C – ethyl alcohol is poured into a vessel with a layer of insulation. Then small portions of solid carbon dioxide are introduced into the alcohol.

Before determination, the tested diesel fuel is dehydrated, for which it is shaken for 10...15 minutes. with freshly calcined and crushed sodium sulfate or with granular calcium

chloride. Then the fuel is settled and filtered. Dehydrated diesel fuel is poured into test tube 2 and closed with a cork with an inserted thermometer 4. The test tube is inserted into test tube-coupling 1, which is previously filled with 1 ml of sulfuric acid to absorb moisture from the air and prevent the appearance of water on the walls of the test tube-coupling during cooling.

The assembled device is lowered into the cooling mixture and installed strictly vertically. Starting from a temperature that is 9°C higher than the expected solidification temperature of diesel fuel, after every 3°C the test tube is removed from the tube-coupling and the mobility of the diesel fuel is monitored at an incline. During the experiment, diesel fuel is mixed with a stirrer 5.

The solidification temperature of the tested diesel fuel is taken as the temperature at which the fuel remains stationary in a horizontally located test tube for 5 seconds. The solidification temperature determines the storage conditions, because at this temperature it is impossible to transfer fuel from one tank to another.

### **5.3 WATER AND MECHANICAL IMPURITIES**

The presence of water and mechanical impurities in diesel fuel is one of the main reasons for failure of fuel equipment. Water and mechanical impurities can get into the fuel, starting from the way it passes from the oil refinery to its use in the engine. Most mechanical impurities are very hard and cause increased wear of engine parts. Impurities for high-pressure fuel pumps, injector pumps, and injectors are especially harmful. In precision pairs, the gap is 1.5...3 μm, so even a small amount of mechanical impurities, the size of which can be compared with the gap of plunger pairs, causes their intensive wear.

Mechanical impurities in diesel fuel increase tar formation, cause clogging of the fuel supply system, increase the amount of deposits and soot on the nozzles, in the combustion chamber and on other elements, impairing the reliability and durability of the fuel supply system, significantly increasing fuel consumption and exhaust gas smoke. When using dirty fuel, the service life of fuel equipment is reduced by 5...6 times.

Before refueling the car, the fuel must stand for at least 10 days. At the same time, the purity of different layers of fuel will be different. Even with a 10-day standstill, small particles of mechanical impurities remain in the lower layers of fuel, which pose the greatest danger to fuel equipment. Cars must be refueled with fuel from the upper layers. The content of mechanical impurities in diesel fuel is not allowed.

It is not allowed to use fuel containing water, as it leads to malfunctions of the engine, the impossibility of starting it, increased corrosion, and increased soot formation.

The purity of diesel fuel is evaluated by *the filtration coefficient*, which determines the efficiency and reliability of the engine, especially its fuel equipment. *The filtration coefficient is found as the ratio of the time of filtration through a paper filter at atmospheric pressure of the tenth portion of the filtered fuel to the first.* Fuel filtration is affected by the presence of mechanical impurities, water, resinous substances, and naphthenic acids. For diesel fuel of different brands, the filtration coefficient ranges from 2 to 3.

As a result of microbial contamination of fuel, engine failure is possible due to clogging of fuel lines and fuel filters. Diesel fuel contains 45 different types of bacteria and about 20 different types of fungi. Fuels are contaminated in tanks and pipelines, which

are alternately used for different petroleum products. Microbial fuel contamination is especially common in tanks with water at the bottom. Contamination of diesel fuel occurs through the penetration of bacteria and fungi from the outside with air or water, or as a result of contact with previously contaminated fuel. Microorganisms spread along the water-fuel interface and live in the water, feeding on the fuel.

As bacteria and fungi develop, the quality of the fuel deteriorates sharply, unfavorable changes in the fuel occur, which cause its turbidity, microbiological corrosion, sediment formation, clogging of filters and pipelines, decomposition of additives and additives.

Turbidity of fuel occurs due to an increase in its water content due to the formation of by-products of the life of microbes - surface-active substances that increase the solubility of water in fuel. Microbiological corrosion occurs as a result of the release of hydrogen sulfide by bacteria, which dissolves in fuel and causes severe pitting of fuel tanks and pipelines. Microorganisms settle at the bottom of tanks and form a layer that promotes microbiological corrosion. The sediment is contaminated with viable microbes and fungi and is a constant source of infection. Various additives and additives in diesel fuel, especially containing nitrogen and phosphorus, are assimilated by microorganisms, and their effectiveness decreases.

To disinfect diesel fuel and prevent its contamination, an additive based on isothiazolone derivatives and others was developed.

#### **5.4 ASSORTMENT OF DIESEL FUELS**

Oil refineries in Ukraine produce diesel fuel according to DSTU 7688:2015. This standard provides for the following classification of diesel fuels:

- according to the climatic conditions of use, the following brands of diesel fuel are established: S - summer, used at an air temperature not lower than 5 °C; W – winter, used at air temperatures from 5 °C to minus 20 °C; Ark – arctic, used at air temperatures lower than minus 20 °C.

- according to the level of environmental safety, the following environmental classes of diesel fuel are established: Euro 3, Euro 4, Euro 5.

The conventional mark of diesel fuel must contain:

- letters DF (designation of diesel fuel);
- letter designation of the brand (S, W, Arc);
- ecological class symbol (Euro 3, Euro 4, Euro 5);
- a symbol for determining the content (volume fraction) of methyl/ethyl esters of fatty acids (B0 – in case of their absence; B5 – not more than 5%; B7 – more than 5% and not more than 7%).

An example of the marking of diesel fuel of the summer environmental class Euro 4 with a content of methyl/ethyl esters of fatty acids of more than 5% and not more than 7%: "Diesel fuel DF-S-Euro 4-B7 according to DSTU 7688:2015".

The fuel label may contain the trademark (trademark) of the manufacturer.

An example of the marking of "XXX" brand diesel fuel of the arctic environmental class Euro 3 without the content of methyl/ethyl esters of fatty acids:

"Diesel fuel XXX-DF-Ark-Euro3-B0 according to DSTU 7688:2015".

## **5.5 TOXICITY OF EXHAUST GASES OF DIESEL ENGINES**

The operation of cars is accompanied by environmental pollution with emissions of toxic gaseous and solid substances. Engine exhaust and crankcase gases are the main source of pollution.

Toxic emissions negatively affect the health of people and animals, cause damage to plants, accelerate the corrosion of metals and the destruction of building structures. Nitrogen and sulfur oxides, soot, aldehydes, carbon monoxide, hydrocarbons, benzopyrene, and ammonia cause the greatest harm to humans, animals, and plants. The smell and lachrymatory effect of exhaust gases are also of great importance. Toxic products of fuel combustion accumulate in soil, water, plants and buildings. Being in the air, they are partially transformed into other compounds that can be more toxic than the original products.

## **5.6 CONTROL QUESTIONS**

1. What causes increased corrosion and wear of engine parts?
2. What characterizes fuel acidity and what does it affect?
3. What does the corrosiveness of diesel fuel depend on?
4. What are cloud point and pour point?
5. How do depressant additives work?
6. What does the filter coefficient evaluate and determine?
7. What types of diesel fuel do you know?
8. What properties should environmentally friendly diesel fuel have?

## LECTURE 6. ALTERNATIVE FUELS (part 1)

Lecture plan:

- 6.1 Gaseous fuels. General Information.
- 6.2 Liquefied gas.
- 6.3 Natural gas.
- 6.4 Generator gas. Biogas Synthesis gas.
- 6.5 Peculiarities of using gaseous fuels.
- 6.6 Control questions.

### 6.1 GASEOUS FUELS. GENERAL INFORMATION

Gaseous fuels are used in internal combustion engines along with liquid fuels. The automobile industry, based on gasoline cars, serially produces gas cylinders, which are mainly used as urban transport.

The rapid growth of the automobile fleet in cities requires finding ways to reduce the toxicity of exhaust gases. This problem can be partially solved during the transition of cars to gaseous fuel. A significant part of cars in large cities has already been converted to gaseous fuel, which has significant technical, economic and sanitary-hygienic advantages over other automotive fuels. When working on it, more complete combustion of fuel occurs, the toxicity of exhaust gases decreases. So, in the exhaust gases of engines running on liquefied gas, there is approximately 5 times less carbon dioxide and 3...3.5 times less unburned hydrocarbons, compared to the content of these components in the exhaust gases of cars running on gasoline (Table 6.1).

Table 6.1 – Composition of exhaust gases of gaseous fuels and gasoline, g/100 km

Composition of exhaust gases	When using		
	gasoline	compressed gases	liquefied gases
Unburnt hydrocarbons	187,5	131,3	55,0
Carbon dioxide	1250	468,8	256,3
Nitrogen oxides	250	118,8	118,8

When working on gaseous fuel, carbon deposits and engine oil consumption are reduced. In addition, gaseous fuel has high octane numbers and heat of combustion. Table 6.2 shows some indicators of the quality of gaseous hydrocarbons.

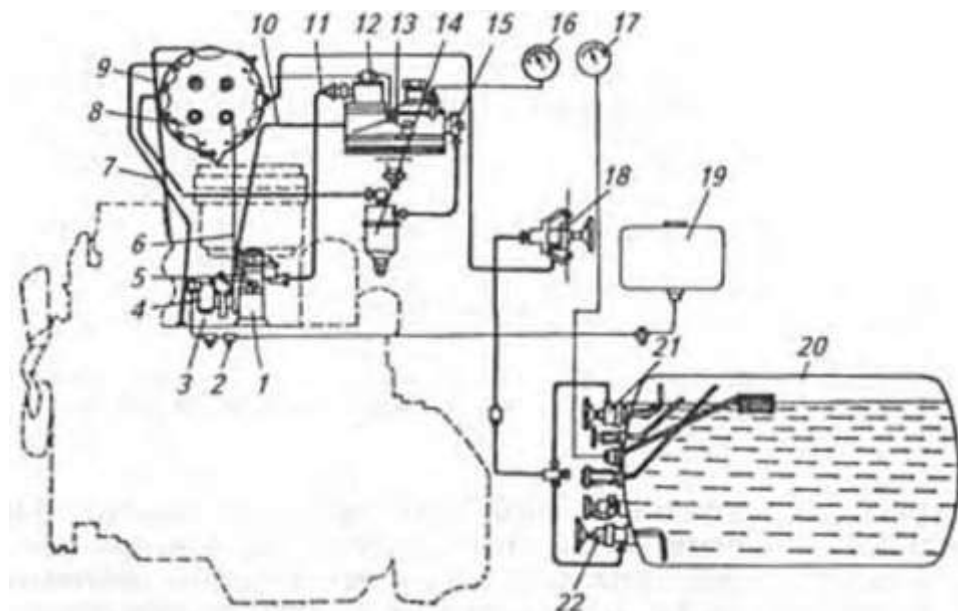
Table 6.2 – Indicators of gaseous hydrocarbons

Hydrocarbon	Relative density in air	Critical temperature <sup>1</sup> , °C	Boiling temperature, °C	Lower heat of combustion, МДж/м <sup>3</sup>	Octane number according to the research method
Methane	0,554	– 82,1	– 161	35,8	120
Ethan	1,138	32,3	– 94	63,7	116,3
Propane	1,523	95,7	– 44	91,2	111,6
Propylene	1,453	91,6	– 47	86	102,6
n-Butane	2,007	152,8	– 0,5	118,6	95,8
Butylene	1,937	144,0	– 5	113,5	91,4
Isobutane	2,007	134,0	– 11,7	118,6	102,1

<sup>1</sup>Temperature above which the gas cannot be liquefied under any pressure.

The raw material for obtaining gaseous automobile fuel is natural and accompanying gases released during oil production, as well as gases from oil refineries, petrochemical plants, etc. The main components of natural gases: methane, in smaller quantities ethane, propane, butane. **Hydrocarbons, the critical temperatures of which are higher than the normal operating temperatures of cars, easily turn into a liquid state under a certain pressure and are therefore called liquefied.** These hydrocarbons include **propane and butane.** To convert propane into a liquid state, a pressure of 0.85 MPa is required, and for butane - 0.2 MPa at 20 °C. **Hydrocarbons, the critical temperatures of which are lower than the normal operating temperatures of cars, are used, as a rule, in a compressed state and are called compressed.** These include **methane and ethane.** To convert methane into a liquid state, temperatures below minus 82°C are necessary. At a temperature of minus 161°C, methane turns into a liquid state at atmospheric pressure. At temperatures above minus 82°C, it cannot be converted into a liquid state under any high compression pressure.

Gas cylinder cars differ from basic gasoline models by a higher degree of compression of the working mixture in the engine and the presence of a gas cylinder installation. Constituent parts of the gas cylinder installation: fuel supply equipment that provided evaporation, pressure reduction and gas dosing in accordance with the engine's operating mode; cylinders for gas transportation and storage (Fig. 6.1).



- 1 - spacer; 2 - filter-settler; 3 - fuel pump; 4 - carburetor; 5 - gas mixer. 6, 10 - tubes;  
 7, 9, 11 - hoses; 8 - evaporator; 12 - dosing device; 13 - gas reducer; 14 - gas filter;  
 15 - mesh filter; 16 - manometer; 17 - liquefied gas level indicator in the cylinder;  
 16 - main valve; 19 - fuel tank; 20 - cylinder; 21 - vapor phase outlet valve;  
 22 - dispensing valve of the liquid phase.

Figure 6.1 – Scheme of the gas cylinder installation of the car

However, gaseous fuel has some disadvantages. The main disadvantage is that gas filling stations are more complicated and expensive compared to liquid fuel filling stations. This deters the use of gas cylinder cars in long-distance transportation. When converting gasoline engines to gaseous fuel without additional modifications, the energy

performance of the engine deteriorates: the engine power decreases by 6...8% when operating on liquefied gas and by 18...19% when operating on natural gas due to a decrease in the filling factor, lower heat combustion of gas-air mixture and others.

## 6.2 LIQUEFIED GAS

Car engines use liquefied gases obtained in the process of oil distillation. These gases have a high heat of combustion, are transportable, and can be transported by any type of transport. When working on liquefied gases, the engines have high technical and economic and sanitary and hygienic indicators. Liquefied gases pass from a gaseous state (vapor phase) to a liquid (liquid phase) at ambient air temperature and relatively low pressures.

Liquefied gas of the brands PA – automotive propane and PBA – automotive propane-butane are produced for road transport. Physico-chemical parameters of these gases are given in table 6.3.

Table 6.3 – Physico-chemical indicators of liquefied automobile gases of PA and PBA brands

Indicator	PA	PBA
Mass fraction of components, %:		
the sum of methane and ethane	Not normalized	
propane	90 ± 10	50 ± 10
the amount of hydrocarbons is higher C <sub>4</sub>	Not normalized	
the sum of unsaturated hydrocarbons, no more	6	6
Saturated vapor pressure, excess, MPa, at temperature:		
+45°C, no more	—	1,6
-20°C, no more	—	0,07
-35°C, no more	0,07	—
The mass fraction of sulfur and sulfur compounds, %, no more	0,01	0,01
Including hydrogen sulfide, no more	0,003	0,003

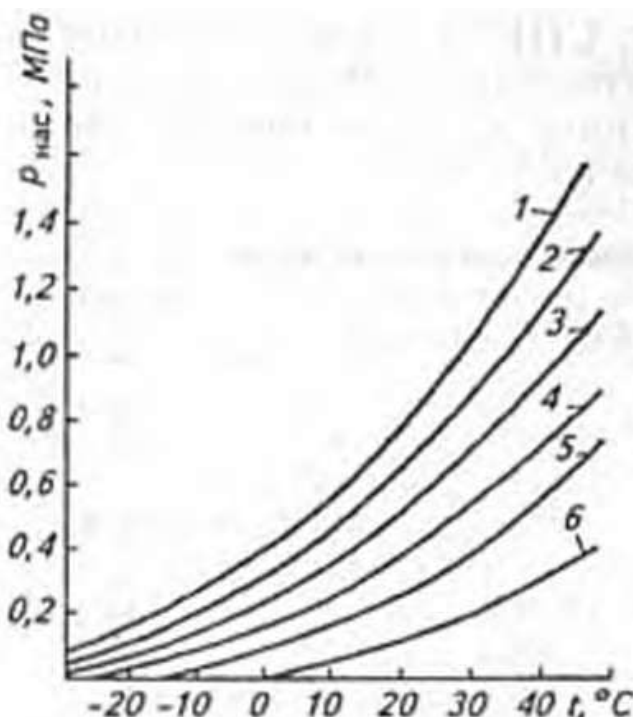
*Note. Gases of both brands have a liquid residue at a temperature of +40°C and do not contain free moisture and alkalis.*

Cylinders with a total capacity of 225 liters, which are designed for a pressure of 1.6 MPa, are included in the power supply system of engines running on liquefied gas.

PBA gas is intended for all climatic regions with an ambient air temperature not lower than -20°C, and PA gas - in the winter period for those climatic regions where the air temperature is lower than -20°C. The recommended temperature interval for the use of PA gas is from -20 to -35°C. In the spring period, in order to fully consume the reserves of liquefied gas, the PA brand is allowed to be used at a temperature of up to 10°C.

The main components of liquefied gas that provide optimal pressure of saturated vapor in the gas cylinder are propane and propylene. Saturated steam pressure significantly affects the operation of the car's gas installation. Figure 6.2 shows the pressure dependence of saturated vapors  $P_{sat}$  of propanebutane mixtures depending on the

temperature  $t$ . Vapor pressure increases with temperature, and propane increases much faster than butane. The more propane in the propane-butane mixture, the higher the vapor elasticity of the mixture. Knowing the pressure of the mixture at a certain temperature, it is possible to estimate the percentage content of propane and butane in it.



1 - propane; 2 - 80% propane + 20% butane; 3 - 60% propane + 40% butane;  
4 - 40% propane + 60% butane; 5 - 20% propane + 80% butane; 6 - butane.

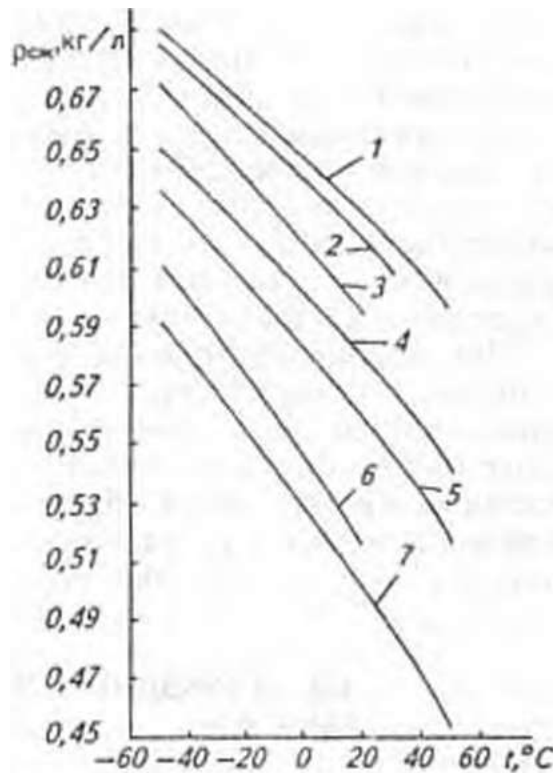
Figure 6.2 – Saturated vapor pressure of propane-butane mixtures versus temperature

The strength of the gas cylinder is determined by the maximum pressure of the saturated vapors of the mixture, and to ensure the normal operation of the fuel equipment, the mixture must have an excess pressure of at least 0.1 MPa. By changing the component composition, winter and summer mixtures are obtained. So, the winter mixture contains 75% propane and propylene, and the summer mixture - 60% butane and butylene. Butane hydrocarbons (butane, isobutane, butylene, isobutylene, etc.) have the highest heat of combustion and are easily compressed.

By the density of the liquid phase, it is possible to judge the energy concentration in a unit volume of liquefied gas, which refers to light liquids, the density of which is 0.5...0.55 kg/l. A distinctive feature of liquefied gases is a higher coefficient of volume expansion than that of liquid petroleum products.

Figure 6.3 shows the change in density of liquefied gases depending on temperature.

For example, the density of propane in liquefied form at  $-10^{\circ}\text{C}$  is 0.54 kg/l, and at  $30^{\circ}\text{C}$  it decreases to 0.48 kg/l. At the same time, the specific volume increases by 11%. This property is taken into account when filling the cylinder with gas, leaving about 10% of the volume for the vapor cushion. If the cylinder is completely filled, that is, there will be no vapor cushion, then even a slight increase in the temperature of the liquefied gas will lead to a sharp increase in the pressure in the cylinder. The pressure increase in the cylinder is approximately 0.7 MPa per degree increase in the temperature of the liquefied gas.



1 - pentane; 2 - isopentane; 3 - butylene and isobutylene;  
4 - butane; 5 - isobutane; 6 - propylene; 7 - propane.

Figure 6.3 – Dependence of density of liquefied gases on temperature

All components of liquefied gas, except for methane and ethylene, are heavier than air, therefore, with a leak, they accumulate in low places (on the floor, in ditches, pits), forming an explosive mixture. Liquefied gases are less flammable and explosive than gasoline vapors. Liquefied gases form explosive mixtures with air with a concentration of propane vapors from 2.1 to 9.5%, isobutane from 1.8 to 8.4%, normal butane from 1.5 to 8.5% by volume at a temperature of 15 ...20 °C.

Self-ignition temperature in air at a pressure of 0.1 MPa (760 mm Hg): propane 466 °C, isobutane 462 °C, butane 405 °C. The maximum permissible concentration in the air of the working area (calculated to carbon): propane 300 mg/m<sup>3</sup>, unsaturated hydrocarbons 100 mg/m<sup>3</sup>.

Liquefied gases have high detonation resistance. For example, the octane number of propane, determined by the motor method, is 96, butane 90. However, some gas components have relatively low octane numbers. So the octane number of butylene is 80, and propylene is 85, as a result of which their content in liquefied gas is limited.

The toxicity of the components of liquefied gases affects the human body indirectly. These gases do not cause direct poisoning, but when mixed with air, they reduce the oxygen content in it and thereby lead to oxygen starvation of a person. Liquefied gases, falling on the human body, cause frostbite, which resembles a burn.

To sense the presence of gas in the surrounding air, it is given a specific smell by adding strongly smelling substances – **odorants**. Among them, **ethylmercaptan** is the most widely used: 2.5 g per 100 liters of liquefied gas. With this degree of odorization, 0.4...0.5% gas in the air can be determined by smell. This gas concentration in the air is non-explosive, as it is only 20% of the lower flammability limit.

### 6.3 NATURAL GAS

Natural fuel compressed gas is used for internal combustion engines. This gas is obtained from combustible natural gas transported by main gas pipelines or city gas networks. At the gas filling compressor station, compression and removal of impurities is carried out using a technology that does not involve changing the component composition.

Table 6.4 shows the physical and chemical parameters of natural gas for internal combustion engines. Main gas components: methane and ethane. Possible impurities of nitrogen, oxygen, hydrogen sulfide, water vapor, others.

The power system of automobile engines running on compressed natural gas includes steel cylinders with a capacity of 50 liters, which are designed for an operating pressure of 19.6 MPa. The temperature of the gas filled into the cylinder should not exceed the temperature of the surrounding air by more than 15°C. Gas can form explosive mixtures with air.

Table 6.4 – Physico-chemical parameters of natural compressed gas

<b>The name of the indicator</b>	<b>Indicator value</b>
Volume lower heat of combustion, kJ/m <sup>3</sup> , no less	31800
Relative density to air	0,55...0,70
Octane number of gas (according to the motor method), no less	105
Content of hydrogen sulfide, g/m <sup>3</sup> no more	0,02
Mercaptan sulfur content, g/m <sup>3</sup> , no more	0,036
The content of mechanical impurities, mg/m <sup>3</sup> , no more	1
Total volume fraction of non-combustible components, %, no more	7
Volume fraction of oxygen, %, no more	1
Water vapor content, mg/m <sup>3</sup> , no more	9

The ignition limits of gas (by methane) in a mixture with air at a temperature of 20°C and normal pressure are 5...15% (by volume). The maximum permissible concentration of hydrocarbons in the air of the working area should be no more than 300 mg/m<sup>3</sup> in terms of carbon, and hydrogen sulfide - no more than 10 mg/m<sup>3</sup>.

The use of compressed gases, especially natural gases, is most profitable in the areas of their extraction and processing, near gas mains, social and gasified cities. Converting these gases into a liquid state under the conditions of car operation requires very high pressures and low temperatures.

Five to eight cylinders with compressed gas are most often installed on cars. The mass of eight cylinders is more than 500 kg, so the power of the car is reduced. The mileage of such a car is approximately two times less compared to the mileage of cars running on gasoline or liquefied gas. This prevents the widespread use of compressed gas during the operation of gas cars.

Compressed gases have increased evaporation, so their increased loss is observed. In addition, they have an increased fire hazard. Nevertheless, natural gas can be used prospectively in a liquid state. Natural gas is the cheapest fuel. It is advisable to use it in cars with isothermal bodies (refrigerators).

When using compressed gases, special attention should be paid to the moisture content, because it causes serious problems in the operation of the power system.

## 6.4 GENERATOR GAS. BIOGAS. SYNTHESIS GAS

**Generator gas.** It is obtained during the processing of solid fuel with a lack of air of about 60% in special devices – gas generators. Coal or brown coal, firewood, peat, briquettes from various agricultural wastes (sawdust, sunflower husks, flax fire, other.) are used as solid fuel. Depending on the type of solid fuel used for gasification, the composition of generator gas varies within the following limits: CO – 25...30%, H<sub>2</sub> – 12...15%, CH<sub>4</sub> – 0,5...3,5%, CO<sub>2</sub> – 5...8%, O<sub>2</sub> – 0,2...0,5%, N<sub>2</sub> – 45...50%.

**Biogas.** It is a methane substitute gas that is formed during the accelerated production of high-quality organic fertilizers, many different designs of anaerobic microbiological reactors have been developed for its production. The cetane content in biogas reaches 70%, and the calorific value of biogas is 20...25 MJ/kg. Biogas can be used in any heating plant, because the wear and tear of engines running on biogas is less compared to the wear and tear of engines running on gasoline.

**Synthesis gas.** Synthesis gas (a mixture of carbon monoxide and hydrogen) produced during some petrochemical processes can be used as a raw material for fuel production. Synthesis gasolines require further processing in order to increase the octane number. Diesel fraction can be used as a high-cetane fuel component (diesel fraction has a high freezing point, which must be taken into account when producing commercial fuel).

Gases from oil refineries and petrochemical plants contain saturated and unsaturated hydrocarbons. The synthesis methods of such gases produce liquid fuels, in particular, high-octane components: alkylates, aromatic hydrocarbons, methyl-tert-alkyl ethers (methyl-tert-butyl with an octane number of 105/M and 118/R and methyl-tert-amyl with an octane No. 99/M and 112/R); gasoline with an octane number of 81/M and 96/R, polymer gasoline with an octane number of 82...85/M and 95...98/R.

## 6.5 FEATURES OF THE APPLICATION OF GASEOUS FUELS

Gaseous fuels have some advantages over gasoline and diesel fuels. Gas cylinder cars are significantly more economical than basic models that run on liquid fuel, mainly due to lower engine oil consumption, increased engine mileage and lower fuel costs.

An increase in the service life of motor oil in gas engines is achieved due to the absence of condensation of fuel vapors on the walls of the cylinder and, in this connection, the absence of oil dilution. Therefore, the service life of the oil during the operation of the gas engine increases by 2...4 times, and the service life of the engine itself – by 1.5...2 times.

In gas engines, the oil film is not washed off the walls of cylinders and pistons, the amount of soot and various deposits on the walls of the combustion chamber and in the piston group is small. As a result, the operating conditions of the engine are improved, and the wear of parts of the connecting rod and piston group is reduced.

Gaseous fuels have high detonation resistance, as a result of which they can be used in internal combustion engines with high compression ratios, and therefore, good technical and economic indicators. Thus, the octane numbers obtained by the research method are: ethane 116.3; propane 111.6; butane 95.8 (see table 6.1).

A significant advantage of gaseous fuel is minor pollution of the environment by toxic components.

During operation of a gas engine, more complete mixture formation and more complete combustion of the working mixture occurs than in gasoline engines. As a result, a very small amount of incomplete combustion products are formed, which are particularly

harmful to human health. Thus, the combustion products of a gas engine operating in idle mode contain 5 times less CO than the combustion products of a gasoline engine in the same mode.

The disadvantage of gas cylinder cars is a complicated fuel supply system. There are also increased fire requirements for premises during maintenance and repair of gas cylinder installations due to possible gas leaks.

All over the world, the fleet of cars running on oil and liquefied natural gas is constantly growing. Liquefied natural gas can be used to produce environmentally friendly gasoline and diesel fuel with a low content of aromatic hydrocarbons and solid particles. However, this is not always economically justified.

In some countries of the world, the production of dual-fuel cars that run on both liquid and gaseous fuel has been established. They also produce cars that use hydrogen.

It should be noted that in the USA, Great Britain, Germany and other countries, similar work is underway to create vehicles on fuel cells that run on hydrogen.

## **6.6 CONTROL QUESTIONS**

1. What are the composition and properties of liquefied gases?
2. Tell us about compressed natural gas.
3. Tell us about generator gas.
4. Tell us about biogas. How is it obtained and used?
5. Tell us about synthesis gas.
6. List the features of the use of gaseous fuels.
7. What are the main operational and technical properties of gas fuels?
8. Name promising environmentally friendly fuels.

## LECTURE 7. ALTERNATIVE FUELS (part 2)

Lecture plan:

7.1 Alcoholic fuels.

7.2 Biofuel.

7.3 Hydrogen as a fuel.

7.4 Furnace fuel oils.

7.5 Stove household fuel.

7.6 Solid fuel.

7.7 Control questions.

### 7.1 ALCOHOLIC FUELS

In recent years, there has been an increased interest in the use of alcohols as substitutes for petroleum fuels or as an additive to them. Among alcohols, methanol ( $\text{CH}_3\text{OH}$ ) and ethanol ( $\text{C}_2\text{H}_5\text{OH}$ ) have the greatest practical importance today. In terms of their physico-chemical and operational parameters, these fuels most fully correspond to the characteristic features of modern internal combustion engines (Table 7.1).

Table 7.1 – Physico-chemical properties of petroleum and alcohol fuels

Indicator	Gasoline	Diesel fuel	Methanol	Ethanol
Lower calorific value, MJ/kg	44,4	42,7	19,95	27,72
Density at 20°C, kg/m <sup>3</sup>	710..760	830...860	796	794
Kinematic viscosity, mm <sup>2</sup> /s at 20°C	0,52...0,63	1,5...6,0	0,758	1,52
Boiling temperature, ° C	35...215	160...360	65	78
Ignition temperature, ° C	430	210	470	420
Cetane number	–	≥45	3	8
Octane number (motor method)	76...98	–	95	94

The prospect of using alcohols, especially methanol, is determined by the real possibility of their extraction using a certain production technology based on a diverse raw material base. Methanol can be extracted from coal, natural gas and other sources, ethanol – from renewable plant raw materials. Alcohols can be transported, stored and distributed in the same way as petroleum fuels, they are more acceptable from an environmental point of view, because when they are used, the content of pollutants in the exhaust gases is lower.

One of the main advantages of alcohols is high detonation resistance, which makes it possible to increase the degree of compression, and therefore the indicator efficiency of the engine. Compared to petroleum fuels, alcohols are characterized by more stable combustion, thanks to which they can work on lean mixtures ( $\alpha=1.5...1.6$ ), which also increases engine efficiency. Increasing the power of engines running on alcohol is also facilitated by an increase in the filling factor due to their high latent heat of vaporization and higher density of alcohol-air mixtures.

At the same time, unlike hydrocarbon fuels, alcohols have a lower heat of combustion, which causes their higher volumetric consumption. Due to the high heat of

vaporization, their starting properties are lower than those of gasoline. They are also corrosive and aggressive to metals and toxic.

These properties of alcohols determine the perspective of the main directions of development of both motor engineering and fuel production.

Extensive experience in the use of ethanol instead of gasoline has been accumulated in Brazil, where there are significant raw materials for its extraction – sugar cane. Nowadays, at the current level of development of motor engineering, the use of additives to gasoline has become quite real. It has been established that when adding 2...3% ethanol, no special adjustment of the engine is required. In the USA and other developed countries, a fuel called Gasohol (a mixture of 10% ethanol and 90% gasoline) is already used. Engine efficiency increases by 2...4% when using gasohol.

To organize the operation of the engine on methanol, a rational gasoline-methanol mixture containing 10...15% methanol is installed. Methanol is also a component of an effective additive – methyl tert-butyl ether (MTBE), the use of which will make it possible to eliminate tetraethyl lead from gasoline, and to release catalytic cracking gasoline from the component composition of gasoline, replacing it with a less expensive direct distillation distillate. Unlike methanol and ethanol, MTBE practically does not stratify when mixed with gasoline, has a high octane number and heat of combustion. Therefore, the lower the octane number of the original gasoline to which alcohol is added, the greater the anti-knock effect (Table 7.2).

Table 7.2 – Effect of ethanol on the octane number of gasoline

Alcohol content in a mixture with gasoline, % vol.	Octane number of the mixture	
	№ 1*	№ 2*
0	70	65
5	–	68
10	71,5	72,5
15	–	77
20	73	–

\*Note: Gasoline №1 and №2, to which alcohol is added, have different octane numbers.

## 7.2 BIOFUELS

Motor fuels obtained from renewable, mainly vegetable sources of raw materials are called biofuels. In recent years, considerable attention has been paid to the production and use of biofuels. For the production of this type of fuel, various oil crops (soy, rapeseed, other.) are used, as well as animal fat production waste. Most often, rapeseed oil is used for the production of biofuel, which consists of complex esters of glycerol and higher saturated and unsaturated carboxylic acids.

Rapeseed oil has a high melting point, and therefore it is subjected to hydrolysis to obtain glycerol and a mixture of fatty acids. This mixture is etherified with methanol to obtain methyl esters of fatty acids of rapeseed oil – biodiesel fuel, which can be used as such or in the form of various compositions with traditional petroleum fuel.

The introduction of up to 10% of biodiesel fuel practically does not affect the physicochemical and operational properties of petroleum diesel fuel, with a higher content there is a need to add depressant additives.

The main physico-chemical and operational properties of biodiesel fuel and its mixture with petroleum diesel fuel are given in table 7.3.

Table 7.3 – Properties of biodiesel fuel and its mixtures with oil diesel fuel

Indexes	Petroleum diesel fuel	Biodiesel fuel	The amount of biodiesel fuel in the mixture, %			
			5	20	30	50
Density, kg/m <sup>3</sup> at 15°C	828	884	833	840	848	858
Cetane index	51	51	51	51	51	51
Lower heat of combustion, MJ/l	35,5	32,9	35,3	35,0	34,7	34,2
Viscosity, mm <sup>2</sup> /s at 40°C	2,2...2,9	4,5	2,4	2,6	2,7	3,1
Flash point, °C	73	188	75	76	78	83

In the USA, two types of diesel fuel are offered: B100 with 100% biodiesel fuel and B20 – petroleum diesel fuel with 20% biodiesel fuel.

When using biodiesel fuel and its mixtures with petroleum fuel, there is no need to reconstruct the equipment of reservoirs, tanks, transport communications, in contrast to the use of other types of alternative fuels. The characteristics of a diesel engine when operating on biodiesel fuel and traditional petroleum fuel are practically similar.

Engines that run on biodiesel fuel emit less soot, carbon oxides and are less toxic compared to engines that use oil fuel.

### 7.3 HYDROGEN AS FUEL

Using hydrogen as a fuel requires a longer time to solve a number of problems. This is primarily the placement of hydrogen on a car. The use of hydrogen in its gaseous state requires cylinders of large mass and volume. Liquid hydrogen can be stored in cryogenic devices at temperatures of minus 252.8°C and below. The storage of hydrogen in metal hydride batteries does not allow to accumulate it in sufficient quantity, because the capacity of the batteries is small with a total large mass.

The very high rate of hydrogen combustion causes large thermal and mechanical loads in engine parts. The low energy required for ignition can cause uncontrolled self-ignition of the fuel. Hydrogen is able to penetrate through the thickness of the metal, with an increase in temperature and pressure, the diffusion of hydrogen into metals increases. Liquid hydrogen can cause the decomposition of some metals. The hydrogen-air mixture has a large ignition limit (4...75% vol.) and explosiveness (18.3...74% vol.).

Hydrogen is very different from traditional fuels in terms of physical and chemical quality indicators (Table 7.4). It has the highest heat of combustion of all traditional and alternative fuels, in terms of mass energy density, hydrogen exceeds petroleum fuels by 2.5...3 times, alcohols by 5...6 times. Hydrogen ignites in a mixture with air in a wide range, including an excess air ratio of 10, so hydrogen ensures stable engine operation at all speed modes with a mixture composition from  $\alpha=0.2$  to  $\alpha=5$ . Combustion of hydrogen-

air mixtures occurs almost at a constant volume (in the stoichiometric region); high combustion rates increase the pressure dramatically.

Table 7.4 – Quality indicators of hydrogen and gasoline

Indexes	Gasoline	Hydrogen
Density at 15°C, g/cm <sup>3</sup>	0,7...0,8	0,07
Boiling temperature, °C	30...205	252,8
Solidification temperature, °C	-60...-80	259,1
The heat of combustion is lower, MJ/kg	~ 42,70	76,27
Heat of vaporization, kJ/kg	180...300	450
Coefficient of substitutability in relation to oil fuel, p/p	1	0,57
Storage conditions	Ordinary	-253°C and below

This sometimes provokes backflow of flames into the intake manifold, premature ignition of fuel mixtures. Improving the fuel supply system can eliminate these shortcomings. To reduce the temperature of the operating cycle, it is necessary to improve the design of the hydrogen engine itself.

The exhaust gases of hydrogen engines have a significantly lower number of toxic compounds compared to the toxicity of exhaust gases of gasoline engines.

One of the disadvantages of hydrogen fuel is the increased content of nitrogen oxides in the exhaust gases. Another disadvantage of hydrogen engines is the possibility of formation of H<sub>2</sub>O<sub>2</sub> hydrogen peroxide during hydrogen combustion. Hydrogen peroxide in exhaust gases additionally pollutes the environment. For its decomposition into water and oxygen, additional converters (thermal or chemical) must be installed on cars.

The use of high-octane gasoline requires an increase in the production of high-octane components, and the depletion of natural resources requires the increasing use of various additives to petroleum fuels, but when developing and using alternative fuels, economic and environmental issues should be taken into account, as well as chemotological justification of their effective use.

## 7.4 FURNACE FUEL OILS

Furnace fuel oils, which are products of oil, oil shale and hard coal processing, are used in boiler plants. The main indicator of fuel oil quality – *viscosity* is the basis of its labeling. Viscosity determines the method and duration of draining and filling operations, transportation conditions and the efficiency of nozzles. Viscosity affects the rate of precipitation of mechanical impurities during storage, transportation and heating of fuel oil, as well as the degree of its separation from water (during settling).

*The density* of furnace fuel oils at 20°C ranges from 920 to 1015 kg/m<sup>3</sup>. In combination with viscosity, it determines the conditions for settling fuel oils and precipitation of mechanical impurities. If the density of fuel oil is lower than the density of water, it settles in 100...200 hours; at a density of 980...1010 kg/m<sup>3</sup>, the settling time exceeds 200 hours, and at a density of about 1050 kg/m<sup>3</sup>, the fuel oil is located in the tanks lower than the water and its settling becomes impossible.

**Low-sulfur furnace fuel oils** contains up to 0.5% sulfur, sulfur fuel oil – up to 2%, high-sulfur fuel oil – up to 3.5%. In the process of burning furnace fuel oils, the sulfur compounds contained in it burn with the formation of mainly sulfur dioxide (SO<sub>2</sub>) and a very small amount of sulfur trioxide (SO<sub>3</sub>). These compounds, in the presence of moisture in the flue gases, form acids that cause increased corrosion of metal surfaces of smoke pipes, economizers and other parts of boilers.

Fuel oils of brands 40 and 100, which are intended for boiler installations, are supplied to agriculture. The lower heat of combustion in terms of dry fuel for low-sulfur fuel oil of brand 40 is 40.74 MJ/kg, brand 100 is 40.53 MJ/kg, and for sulfur fuel of both brands it is 39.9 MJ/kg. The solidification temperature of fuel oil grade 40 should be higher than 10°C, and grade 100 should not be higher than 25°C.

### 7.5 STOVE HOUSEHOLD FUEL

Household furnace fuel is obtained from diesel fractions of both direct oil distillation and secondary origin – distillates of thermal, catalytic cracking and coking.

Furnace fuel does not contain hydrogen sulfide, water-soluble acids and alkalis, as well as mechanical impurities (Table 7.5).

Household furnace fuel has a wider fractional composition compared to diesel fuel. The solidification temperature of -15°C makes it difficult to use it at low temperatures. In the period from April 1 to September 1, it is allowed to use fuel with a solidification temperature not higher than -5°C.

Household stove fuel is widely used in agriculture for the operation of steam and water heating boilers, heat generators, grain dryers, etc. When working with household fuel for the stove in the winter period, it is possible to lose its fluidity on the fuel supply line to heat-generating units, as well as clogging of fuel filters with paraffin. Therefore, the tanks in which the furnace fuel is stored, and the tanks from where it comes to the combustion plants, should be placed in insulated rooms. To improve the low-temperature properties of household furnace fuel, depressor additives synthesized on the basis of a copolymer of ethylene and vinyl acetate are used.

Table 7.5 – Characteristics of household furnace fuel

Indicator	Value
Fractional composition:	
10% is distilled at a temperature, °C, not lower	160
90% is distilled at a temperature, °C, not higher	360
Kinematic viscosity at 20°C, mm <sup>2</sup> /s, no more	8
Solidification temperature, °C, not higher than:	
from September 1 to April 1	-15
from April 1 to September 1	-5
Flash point in a closed crucible, °C, not lower	45
Mass fraction of sulfur, %, not more than:	
in low-sulfur fuel	0,5
in sulfur fuel	1,1
Testing on a copper plate	Withstands

Acidity, mg KOH/100 cm <sup>3</sup> of fuel, no more	5
Ashiness %, not more	0,02
Coking property of the 10% residue, %, no more	0,35
Water content	Traces
Color	From light brown to black
Density at 20 °C, kg/m <sup>3</sup>	Not normalized, definition is mandatory

## 7.6 SOLID FUEL

Solid fuel used in agricultural production is divided into natural (fossil coal, peat, wood waste from agricultural production) and artificial (various briquettes, charcoal). Local types of fuel are widely used in different areas of the country. Solid fuel contains a large amount of ballast, which sharply reduces its thermal value.

Fossil coal is of two main types: humus, formed from higher terrestrial plants (mainly wood), and sapropelite, formed from aquatic plants and algae rich in fats and wax. Widespread coal of mixed origin. Depending on the degree of change in organic matter, or on the "chemical" age, coal is divided into brown, stone and anthracite.

Coal is classified according to the size of the pieces: plate - size of pieces over 100 mm, large - 50... 100, nut - 25... 50, small - 13... 25, seeds - 6... 13, stub - less than 6 mm

**Lignite is a brown** earthy or black homogeneous mass that oxidizes and crumbles into powder during storage. Lignite has a high ash content (15...30%) and moisture (15...50%), so the range of its calorific value is very large (8.4...18.8 MJ/kg). It ignites easily and burns with a long, smoldering flame. Lignite is prone to oxidation and spontaneous combustion, so it is recommended to stack it in stacks no more than 2.5 m high and store it for no more than a month to avoid possible spontaneous combustion.

The composition of brown coal is very heterogeneous: carbon – C=65...78%, hydrogen – H=4.3...6.2, oxygen – O=16...27, nitrogen – N=0.7...1.8, sulfur – S=0.4...3.9%. The yield of volatile substances in fuel is 40...50%, and in some types of coal it reaches 60%. It is classified depending on the size of the pieces: brown large, brown nut, brown small, brown seed with a spine and brown ordinary.

**Hard coal** has a black color and differs from brown by a lower content of ash and moisture. The composition of the organic mass of hard coal is also heterogeneous: C=78...90%, H=4...5.8, O=3...15, N=0.5...2, S=1...6, ash – 15...27, water – 4...12%. The lower working calorific value ranges from 20.73 to 31.4 MJ/kg.

There are six grades of hard coal. Coal intended for thermal processing to obtain resin and gas is labeled LF (long-flame) and G (gas). They have more than 35% volatile substances. Coals that are processed to obtain metallurgical coke are marked with C (coking) and F (fatty). Coal used as fuel is denoted by LS (lean sintering) and S (skinny).

Coal, suitable for burning in blacksmith furnaces, is also used. These coals must contain no more than 20% of volatile compounds, a small amount of sulfur, have a heat of combustion of 25...27 MJ/kg and have the ability to sinter, that is, when decomposed without access to air, form coke in the form of pieces, not powder. Such coal is usually called blacksmith's coal.

**Anthracite** is a type of hard coal and contains 96.5% carbon. It has a black color with a grayish tint, has high density and strength. Anthracite contains a small amount of water (3...5%), ash (10...15%) and volatile substances (2...9%). The heat of combustion of anthracite is the highest among fossil coal - 25...27 MJ/kg, sometimes 30 MJ/kg.

**Shales** are characterized by a high content of ash (50...60%) and moisture (15...20%). The combustible part of shale contains a large amount of hydrogen (up to 10%), and the yield of volatile substances reaches 90%, so they ignite easily. The heat of combustion of shale is low and amounts to 5.8...10.8 MJ/kg. In agriculture, shale is used as boiler fuel.

**Peat** was formed as a result of the decomposition of plant residues in conditions of excess moisture and little access to air. If peat was formed from vegetation rich in mineral salts (sedges, reeds, reeds), it is called meadow or lowland. It contains 8...16% ash. If peat was formed from vegetation poor in mineral salts, it is considered mossy or upland, the ash content in it is 2...4%.

There are peatlands of mixed origin, the ash content of which is 7...9%. Peat is a homogeneous mass from yellow to dark brown in color, the humidity of which is 85...95%.

Peat is a reversible colloid, that is, when it dries, it releases water, and when it gets wet, it absorbs it again. If wet peat is dried to a moisture content below 34%, it will turn into an irreversible colloid. Air-dry peat is convenient for transportation. It can be stored in any weather, because it does not change its shape and does not absorb water, but only slightly wets the upper layers. The organic mass of peat is characterized by the following composition: C=55...56%, H=5...6, O=35...40, N=0.5...3, S=0.12...

1.5%. The lowest heat of combustion of combustible mass of peat is about 12.6 MJ/kg. Peat is widely used as fuel for heating plants and household needs, as well as as fertilizer and bedding for livestock.

**Wood contains** more than 60% cellulose, about 30% lignin and about 1% mineral salts. The elemental composition of the organic part of wood: C = 50%, H = 6, O = 43, N = 1%. The main ballast in the fuel of this type is moisture, the content of which in freshly cut wood reaches 50...60%.

Firewood can be dry (humidity less than 25%), semi-dry (25...30%), raw (more than 35%). Firewood harvested in the autumn or winter period and left in the bilberries for at least a year is classified as dry: for semi-dry – at least 6 months; to raw – less than 6 months after felling. The heat of combustion of the wood fuel mass is 18.8...19.2 MJ/kg, but at a humidity of 30% it decreases to 13.3 MJ/kg.

The heat of combustion (kJ/kg) of firewood of different humidity can be calculated by the formula:

$$Q_H^P = 18422 - 50W^P.$$

The heat of combustion of firewood from wood of different species varies within small limits, but the mass of 1 m<sup>3</sup> of hard species is 1.6...1.8 times greater than that of soft species. Firewood is sold to the consumer by volume, not by weight, so preference is given to hard woods. Taking into account the hardness of the wood, firewood is divided into four groups according to the heat of combustion: 1 – oak, hornbeam, ash, maple, beech – their

thermal equivalent TE = 1.2; 2 – birch, larch – TE = 1; 3 – alder, pine, cedar, fir – TE = 0.8; 4 – willow, aspen, poplar, linden – TE = 0.7.

Agricultural waste is used for production and household needs, especially in areas where there are no forests. Waste includes straw, sunflower husks, firewood, sunflower stalks, rice husks, etc. In terms of the composition of the organic mass, this waste is closest to wood.

**Charcoal** is obtained as a result of dry distillation of wood at a normal temperature of 400...450°C without air access. The organic mass of such coal contains 75% carbon, 4% hydrogen, 20% oxygen and nitrogen. Its ash content is about 1%, moisture content is 10%. The lowest calorific value of charcoal is 27 MJ/kg.

**Artificial fuel** is obtained by physico-mechanical methods (sorting, enrichment, drying, briquetting, etc.) and physico-chemical methods (dry distillation, semi-coking, coking, etc.). Briquettes are obtained from agricultural waste using a binder in presses at a pressure of 100...150 MPa (cold briquetting). During the hot briquetting of peat, dust and coal crumbs, the binder is the resin released by them when heated. The pressure of such briquetting is 25...30 MPa, the temperature is 260...320 °C.

## 7.7 CONTROL QUESTIONS

1. What is the main reason for the development of alternative fuels and what are their raw material sources?
2. What are the operational properties of alcohols, ethers and other alternative fuels?
3. In which installations are fuel oils used?
4. Name the brands of fuel oil used in agriculture?
5. In which agricultural installations is household fuel used?
6. What is the heat of combustion of household fuel?
7. What solid fuels are used in agricultural production?
8. What is the composition of brown coal?
9. Name the agricultural waste used for heating industrial premises and household needs.
10. Tell us about obtaining artificial fuel.

## LECTURE 8. MOTOR OILS (part 1)

Lecture plan:

- 8.1 Main types of friction and wear.
- 8.2 Operating properties of motor oils.
- 8.3 Control questions.

### 8.1 MAIN TYPES OF FRICTION AND WEAR

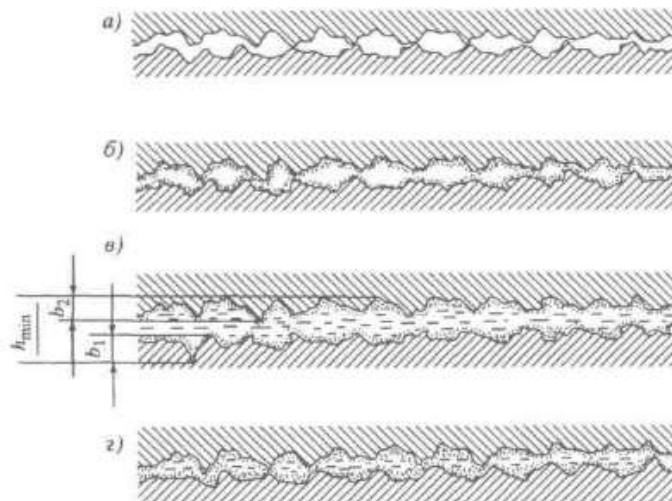
**Friction** (external) refers to the resistance to relative movement that occurs between two bodies in the areas of contact between surfaces tangent to them.

**Reducing frictional losses and reducing the intensity of wear on the surfaces of parts is the main purpose of lubricants.**

According to the nature of the mutual movement of the rubbing parts, two types of friction are distinguished: **friction of rest** – friction of two bodies with a previous displacement and **friction of movement** – friction of two bodies in relative motion.

Motion friction, in turn, is divided by the nature of motion (sliding friction and rolling friction) and by the presence of lubricant (friction without lubrication, boundary friction, and fluid friction). Sliding friction occurs during the movement of touching bodies that have different velocities at the points of contact. In rolling friction, the velocities at the points of contact are the same in magnitude and direction. Rolling friction with sliding occurs during simultaneous rolling and sliding of bodies in contact.

Friction without lubrication is the friction of two solid bodies in the absence of an introduced lubricant on the friction surfaces (Fig. 8.1).



*a - friction without lubrication; б - marginal friction; в - liquid friction; з - mixed friction.*

Figure 8.1 – Types of friction according to the presence of lubricant

Boundary friction occurs when the friction surfaces are separated by a layer of lubricant of such a small thickness (less than  $0.1 \mu\text{m}$ ) that the properties of this layer differ from the bulk properties, and the force of friction depends only on the nature and condition of the rubbing surfaces.

During liquid friction, the lubricating layer completely separates the working surfaces that move one from the other and has a thickness at which the normal volumetric properties of the lubricant are manifested.

The causes of energy consumption for friction without lubrication include:

- mechanical engagement of irregularities (roughnesses) of one rubbing surface with the irregularities of another during their movement;
- forces of intermolecular attraction;
- the phenomenon of welding of rubbing pairs - individual sharp protrusions in conditions of high specific pressures and significant heat release, which can lead to catastrophic wear of parts.

According to the Amonton formula, the sliding friction force  $F$  is proportional to the normal load  $P$ :

$$F=f \cdot P$$

where  $f$  – is the coefficient of friction (its value depends on the type of materials that rub, the quality of their surface treatment and is usually 0.1...0.8, and when rubbing copper on copper – 1.3).

The force of rolling friction is about ten times less than the force of sliding friction of non-lubricated surfaces (the ball or roller contacts the surface at a point or along a line). It is not possible to apply rolling bearings everywhere, and, in addition, in real mechanisms, friction with sliding prevails, which significantly increases the coefficient of friction.

The coefficient of marginal friction is within 0.08...0.15. The limit friction mode is very unstable, it is the limit of the friction unit's efficiency. If the boundary layer is destroyed, the load will exceed the adhesion forces, dry friction occurs at the point of contact and, as a result, burrs, jamming, etc. emergency problems.

It was established that the thickness and strength of the boundary layers depends on the chemical composition of the oil and the additives included in it, the characteristics of the chemical structure and the state of the friction surface. On the other hand, the behavior of the boundary layers depends on the viscosity, and is determined by the interaction of the molecular films of the oil with the metal surface. Films of chemical origin (chemisorption) and physical (adsorption) are distinguished.

The formation of lubricating films by the forces of adsorption is determined by the presence of surface-active substances (SAS) in lubricants that carry an electric charge. They have the ability to adsorb on the liquid-solid interfaces. The ability of lubricants containing SAS to form sufficiently strong layers of oriented molecules on lubricated surfaces is usually called *lubricity or lubricity of oil*. Polar compounds include compounds containing carboxyl groups, alcohols, various ethers, resins, and sulfur compounds. Anti-wear and anti-seize additives are added to some oils to improve their lubricating ability.

The high rate of formation of chemisorbed films ensures their rapid recovery in places of destruction of the boundary layer. Stable chemical films of phosphates, chlorides or sulfides are created on the metal surface due to the presence of the corresponding chemical elements in lubricants. Films of this type also include various soaps formed from higher organic acids found in oil.

Both adsorbed and chemisorbed films, possessing some strength and stability, protect friction surfaces from mechanical and thermal influences, prevent mutual adhesion of rubbing surfaces.

The coefficient of liquid friction is in the range of 0.003...0.03, and the force of friction in this case, which is determined only by the internal friction of the layers in the lubricant, is 50...100 times less than in friction without lubricant. The stability of the lubricating layer required for liquid friction depends on the following factors: the design of the friction unit, the speed of mutual movement of the rubbing surfaces, the specific pressure on them, the viscosity of the lubricating material, the area of the rubbing surfaces, the size of the gap between them, the temperature state friction nodes, etc. Dependencies are illustrated by the processes shown in Fig. 8.2.

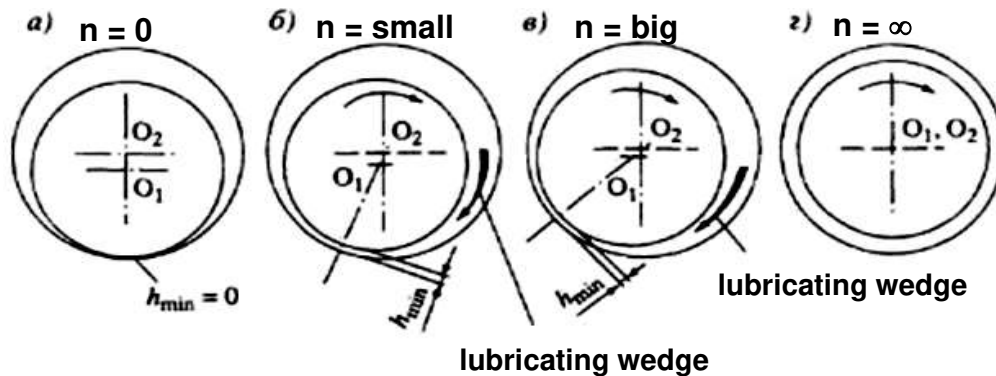


Figure 8.2 – The formation of a lubricating wedge during the rotation of the shaft in the bearing

Rotating in the sliding bearing, the shaft captures the lubricant in the gap, and where the gap is smaller ( $h_{\min}$ ), pressure arises, under the influence of which the shaft seems to float in the lubricating layer, which fills the gap.

With an increase in the number of revolutions, the "wedge effect" of the lubricating layer increases: the shaft increasingly tends to occupy the central position in the bearing (Fig. 8.2), and the value of  $h_{\min}$  increases.

The friction force of a concentrically located shaft in a bearing is calculated by the formula of N.P. Petrov – the creator of the hydrodynamic theory of lubrication. In a simplified version, the force of liquid friction looks like this:

$$F = \eta \frac{Sv}{h},$$

where  $\eta$  – absolute viscosity of the lubricant, N s/m<sup>2</sup>;  $S$  – area of collision of rubbing bodies, m<sup>2</sup>;  $v$  – speed of movement of rubbing surfaces, m/s;  $h$  – thickness of the lubricating layer, m.

To determine the value of the minimum gap in the bearing, the following relationship is established:

$$h_{\min} = \eta \frac{Cv}{P},$$

where  $C$  – coefficient that takes into account the design of the bearing;  $P$  – pressure on rubbing surfaces.

Maintaining regularity:

$$h_{\min} \triangleright 1,5(\delta_1 + \delta_2)$$

where  $\delta_1$  and  $\delta_2$  – the maximum heights of protrusions on the friction surfaces (Fig. 8.1, c) ensure stable and reliable liquid friction.

**For any pairs of rubbing surfaces, the viscosity of the lubricant should be the lowest, but at the same time provide liquid friction.** So, for the crankshaft bearing of internal combustion engines, it should be at least 4-5 mm<sup>2</sup>/s. In real operating conditions, marginal friction may occur, and when starting the engine, at high operating temperatures and loads, semi-fluid friction may occur. It is understood as such a condition when the lubricant in the gap between the rubbing pairs is not enough to fully ensure liquid friction. With this type of friction, the lubricating layer between the rubbing surfaces is partially destroyed, as a result of which marginal (dry) friction occurs in individual places of contact of the friction surfaces. In this case, the lubricant, which has a high lubricating capacity, maximally reduces friction and wear, and also prevents seizing of the parts that rub.

A semi-fluid type of friction is often observed (for example, a piston-cylinder). Under certain conditions (starting and stopping the engine, sudden fluctuations in speed and load, high temperature and specific pressure, insufficient oil viscosity and its supply), friction units designed to work with liquid lubrication are forced to work with semi-liquid lubrication for some part of the time. Liquid friction is often also disrupted when abrasive mechanical impurities get into the oil.

**Wear of rubbing surfaces** – is a change in the dimensions of parts as a result of separation of material from the friction surfaces and as a result of residual deformation of the surface layer. The following types of wear are distinguished (according to the nature of the destruction of parts): mechanical, molecular-mechanical and corrosion-mechanical.

**Mechanical wear** that occurs as a result of mechanical influences is divided into abrasive, hydroabrasive, gaseous, erosive, fatigue, and cavitation.

Abrasive wear is the most common. It is the result of friction on the surface of harder particles, such as wear products, soot, dust, etc. Even a small amount of abrasive particles entering the engine can lead to very rapid wear of the rubbing parts.

Water-abrasive wear, like gas-abrasive wear, is the result of the action of solid particles captured by liquid or gas, respectively.

Fatigue wear is the result of repeated deformation of microvolumes of the material, due to which cracks appear and the separation of particles occurs.

Erosive wear is observed when a liquid or gas friction surface acts on it.

Cavitation wear occurs under cavitation conditions.

When mechanical wear is supplemented by the influence of molecular or atomic forces, this type of wear is called **molecular-mechanical wear**. In this case, there is a local connection (welding) of two solid bodies, the transfer of metal from one surface to another with a deep extraction of metal.

Hence the jamming of parts and burrs.

**Corrosion-mechanical wear** – is defined as the effect of such aggressive substances on rubbing surfaces as chemically active gases, acid impurities of lubricants and other materials, with subsequent mechanical abrasion of damaged surface areas.

The following can be attributed to the reasons that depend on the occurrence of any type of wear and tear and its intensity:

- influence of material properties of friction parts;
- design and manufacturing technology of a unit or part;
- mode of operation;
- conditions of operation of cars;
- quality of fuel and especially lubricant.

***The main functions performed by lubricants in various car units are to reduce friction and wear of rubbing parts.***

During engine operation, different lubrication modes can be observed (Table 8.1)

These modes are implemented under certain conditions that depend on such parameters of the lubrication process as the viscosity of the oil, the speed of movement of the moving surfaces, and the applied specific load.

Table 8.1 – Engine lubrication modes

Lubrication modes	Coefficient of friction
Liquid (hydrodynamic)	0,002 – 0,01
Semi-liquid (mixed)	0,01 – 0,2
Borderline: lubricated surfaces	0,05 – 0,4
unlubricated surfaces (oxidized)	0,2 – 0,8

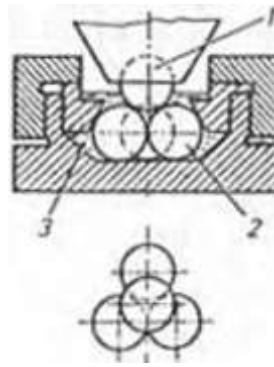
## 8.2 OPERATING PROPERTIES OF MOTOR OILS

Engine oil must perform its functions reliably and for a long time, providing a given engine resource. ***The main functions of engine oil*** in engines are to reduce friction between the surfaces of rubbing parts; reduction of wear of friction surfaces and prevention of their sticking; cooling parts; additional sealing of piston rings, which reduces the breakthrough of gases from the combustion chamber into the engine crankcase; protection of parts from corrosion and contamination with carbon deposits.

The operational properties of motor oils include primarily those that depend on frictional energy losses, wear of rubbing surfaces, the formation of deposits in the engine, corrosion of parts and starting the engine at low temperatures. The main ones are: lubricating and visco-temperature properties, thermo-oxidative stability, detergent, antioxidant and anti-corrosion properties.

***Lubricating properties.*** This name combines several properties of oils that affect the processes of friction and wear of surfaces of rubbing parts in engines. The main ones are: anti-friction – affect energy losses during surface friction; anti-wear - reduce the wear of the surfaces of parts that rub under moderate loads; anti-seize – protect friction surfaces from seizing under conditions of high loads. The main indicator of the lubricating properties of oils is viscosity. In addition, it is the main parameter of motor oils by which they are labeled and classified.

Antiwear properties of oil depend on its chemical composition and viscosity-temperature characteristics, as well as on the quality of additives. The presence of abrasive impurities in the oil significantly affects the wear of rubbing surfaces. The tribological characteristics of oils – ***the burr index***, the critical load and the wear index under constant load are determined according to GOST 9490-75 on a four-ball friction machine (Fig. 8.3).



1 - upper ball; 2 - lower ball; 3 - researched oil.

Figure 8.3 – Four-ball friction machine

A vertical load is applied to ball 1 fixed in a spindle rotating at high speed. The friction assembly is placed in a vessel with oil. As a result of friction, traces of wear are formed on the balls: a stripe on the top, and spots on the bottom. Estimated indicators of the oil's lubricating properties are: wear spot diameter ( $D_s$ ), critical load ( $L_k$ ), welding load ( $L_w$ ) and burr index ( $I_b$ ).

The most reliable method of evaluating anti-wear and anti-seize properties is testing oil in real engine friction nodes. During the test, the anti-wear and anti-seize properties of the oil are evaluated by the loss of mass of piston rings, seizing or pitting of cams and pushers, linear wear of these parts and cylinders, and the condition of the friction surfaces.

**Viscosity-temperature properties.** The quality of lubrication of the surfaces of rubbing parts and their wear depend on the viscosity of engine oil at operating temperatures in the engine. The viscosity of motor oil, in turn, depends on the temperature, as it increases, it decreases, and as it decreases, it increases (Fig. 8.4). The intensity of the change in viscosity with a change in temperature in different motor oils is different. The steepness of the viscosity-temperature curve is estimated by the viscosity index.

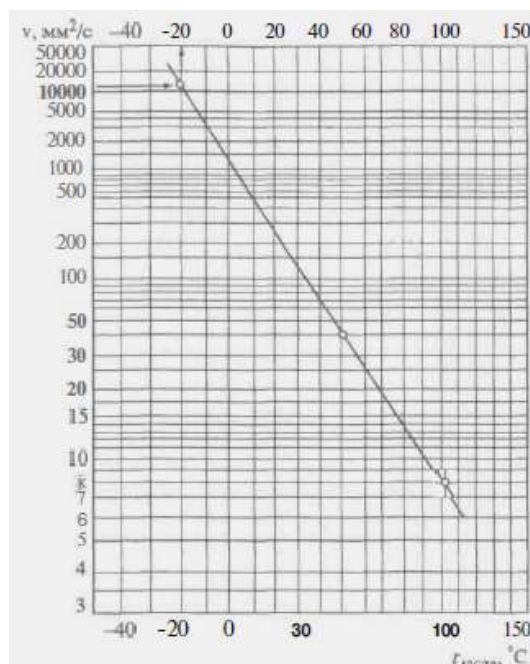
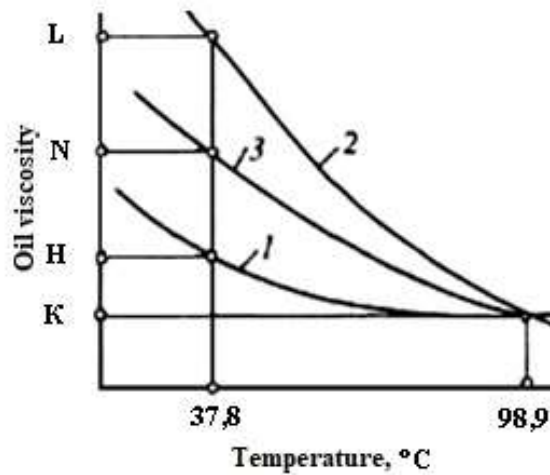


Figure 8.4 – Nomogram for determining viscosity at different temperatures

**The viscosity index** characterizes the degree of change in viscosity depending on the temperature of the oil, or the flatness of the viscosity-temperature curve of the oil. The viscosity index of oils is determined in conventional units (Fig. 8.5), by comparing the viscosity curves of the tested oil and two reference oils, one of which has a very gentle curve – its viscosity index is taken as 100, and the other - a steep curve - the viscosity index is taken as 0. Reference oils have the same viscosity as the tested oil at a temperature of 98.8°C.



*1 - reference oil with good viscosity-temperature properties; 2 - reference oil, with poor properties; 3 - tested oil.*

Figure 8.5 – Scheme for estimating the viscosity-temperature properties of oil by viscosity index

The higher the viscosity index, the better the technical and operational properties of motor oils. The viscosity index is found using the appropriate formulas or nomogram (Fig. 8.6).

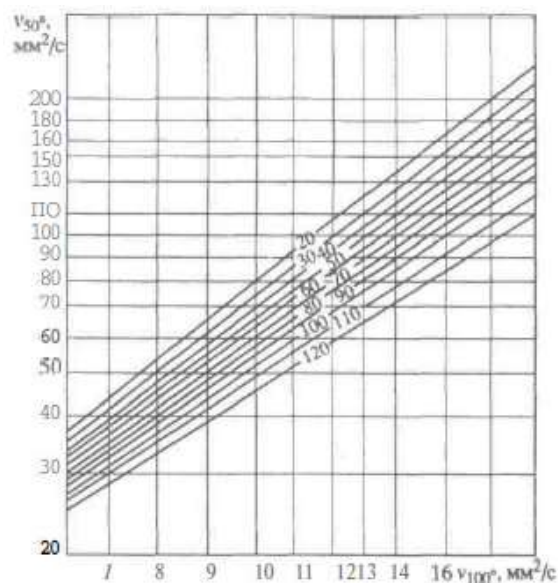


Figure 8.6 – Nomogram for calculating the oil viscosity index

The viscosity index is determined by the formula:

$$IB = \frac{L - N}{L - H} 100,$$

where  $N$  – is the viscosity value at a temperature of 37.8°C for the oil under study, and  $L$  and  $H$  for reference oils.

The viscosity-temperature curve of the tested oil is usually located between the curves of the reference oils. First, the kinematic viscosity of the tested motor oil is determined at 40 and 100 °C. Then, taking into account these values, the viscosity index of the oil is determined by the nomogram or formulas.

**Thermo-oxidative stability.** During engine operation, engine oil undergoes profound changes that lead to changes in physical and chemical properties. The result of such transformations is the accumulation of neutral products in the oil in the form of resinous substances, asphaltenes, carbenes and other compounds of deep oxidation, as well as acidic substances in the form of organic acids, oxyacids, estolides, etc. Oil oxidation products contribute to the formation of varnish and soot on the parts of the piston group, which can lead to coking of the piston rings. **Engine oil should have high thermal oxidation stability**, i.e. it should not form varnish deposits on the surfaces of the piston group of the engine under the influence of high temperature.

The definition of thermo-oxidative stability is as follows. Engine oil, which is on the metal surface in the form of a thin layer, is heated, as a result of which its mass decreases due to the evaporation of volatile substances. The residue obtained on the metal surface is divided into the working fraction and varnish.

Figure 8.7 shows the change in motor evaporation, the tendency to form varnish and the amount of the working fraction of motor oil at a constant temperature of 250 °C, depending on the time of heating on the metal surface.



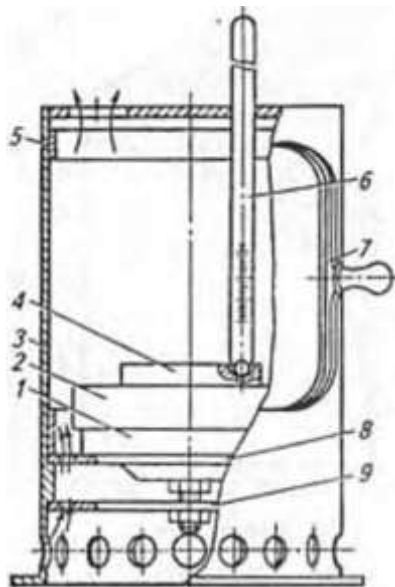
Figure 8.7 – Changes in motor evaporation, tendency to varnish and working fraction of motor oil at constant temperature

As can be seen from the figure, with an increase in the heating time, the motor evaporation and tendency to varnish formation increase, and the amount of the working fraction, that is, the oil that performs the function of a lubricant, decreases.

Thermo-oxidative stability of motor oil is the time (in minutes) during which the tested oil at a temperature of 250°C turns into a varnish residue consisting of 50% working fraction and 50% varnish.

The method of determining the thermo-oxidative stability on the evaporators of the varnish-forming thermostat is used to conditionally assess the tendency of oils to form varnish deposits on engine parts (in the area of piston rings) and to evaluate the effectiveness of additives that reduce varnish formation.

The varnish former for determining thermo-oxidative stability is shown in Figure 8.8. It consists of an electric heating element 1, a plate 2 and a steel disc 4, which is heated by element 1. The temperature of the disc is monitored using a thermometer 6. The device is equipped with a movable glass door 7.



1- electric heating element; 2 - heating plate; 3 - metal case; 4 - disc;  
5 and 9 - upper and lower covers; 6 - thermometer; 7 - movable glass door; 8 - overlay.

Figure 8.8 – Lacquer former for determination of thermo-oxidative stability

A temperature of 250°C is set in the lacquer former. Four evaporating steel plates are placed on the steel disc, each of which contains 0.035...0.04 g of the tested oil. When the oil in the plates oxidizes, which is determined by the change in the color of the oil film, one plate is removed from the disc, and the others are removed at 10-minute intervals. After cooling, the plates are weighed, the working fraction is extracted from the remaining oil with petroleum ether (one or another substance is extracted from the mixture with the help of a suitable solvent). Then the plates are weighed again. This is how the quantitative content of the working fraction and varnish is determined.

Evaporation rate  $H_T^\tau$  (%) of the tested oil at temperature  $T$  during time  $\tau$  is calculated according to the formula:

$$I_T^\tau = \frac{m_1 - (m_3 - m_2)}{m_1} 100,$$

where  $m_1, m_2, m_3$  – weight of the suspension of oil, clean evaporator before the experiment, and evaporator with oil residue after evaporation in the lacquer former, respectively, g.

The mass part of the working fraction  $P\Phi_T^\tau$  (%) of the studied oil at temperature  $T$  during the time  $\tau$  is found by the formula:

$$P\Phi_T^\tau = \frac{m_3 - m_4}{m_1} 100,$$

where  $m_4$  – mass of the evaporator with the varnish residue after extraction, g.

The arithmetic average of two tests is taken as the evaporation and working fraction of the tested oil. The difference between parallel obtained results should not exceed 10% of the average value.

The mass fraction of varnish  $J_T^\tau$  (%) at temperature  $T$  over time  $\tau$  is calculated by the formula:

$$J_T^\tau = \frac{m_4 - m_2}{m_1} 100.$$

Based on the obtained data, a graph of changes over time in the quantities of the working fraction and varnish in the tested oil is constructed (Fig. 8.9).

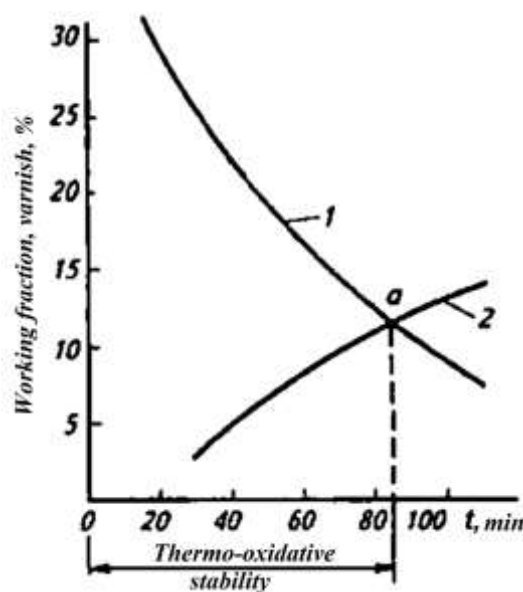
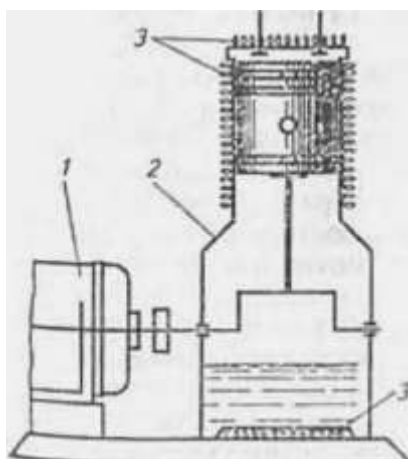


Figure 8.9 – Change over time in the quantitative content of the working fraction (1) and varnish (2) in the tested oil

From the point of intersection of the curves, a perpendicular is lowered to the abscissa axis and the value of thermo-oxidative stability in minutes is obtained. ***The higher the thermo-oxidative stability of the oil, the slower its oxidation in a thin layer at high temperature, the higher the quality of the oil and the lower the danger of rings burning.***

***Detergent-dispersing properties.*** They characterize the ability of the oil to reduce the formation of carbon deposits and precipitation on engine parts and to maintain pollution products in a suspended state. The higher the washing-dispersing properties of motor oils, the more pollution and oxidation products are retained in the working oil without precipitation. And the less varnish deposits are formed on the pistons, and on other parts - grease-like deposits of gray or black color, during the operation of the internal combustion engine. When a special (detergent) additive is added to the oil, its tendency to form varnish and other deposits is sharply reduced. Even after long-term operation, the engine parts are completely clean, as if they were recently washed. This is where the terms "detergent additives" and "detergent properties of oils" originated. These terms are not entirely accurate, because the oil with a detergent additive in the composition does not wash off the varnish from the parts, but prevents its formation on them.

The cleaning properties of motor oils are determined by the intensity of varnish formation on the surface of the piston on the PZV installation (Fig. 8.10).



1 - электродвигун; 2 - одноциліндровий двигун; 3 - електронагрівальні елементи.

Figure 8.10 – The schematic diagram of the PZV installation

The installation consists of a single-cylinder four-stroke engine 2, an electric motor 1 and a control panel. The aluminum piston is equipped with two compression rings and two oil rings. The necessary temperature regime is maintained by electronic heating elements 3. The test conditions are as follows: 250 ml of the tested oil is poured into the engine crankcase; engine crankshaft rotation frequency  $2500 \text{ min}^{-1}$ ; the temperature of the cylinder head is  $300^\circ\text{C}$ , the oil in the crankcase is  $125^\circ\text{C}$ , and the air at the outlet is  $220^\circ\text{C}$ . Duration of the test is 2 hours.

After the test, the device is disassembled and the cleaning properties of the oil are evaluated according to the amount of varnish on the side surface of the piston on a seven-point color scale. If the piston is clean, the oil gets a score of 0, and if it is heavily contaminated with varnish, it gets a score of 6.

**Antioxidant properties.** They characterize the oil's resistance to oxidation. It is impossible to completely prevent oil oxidation due to harsh operating conditions. The process of motor oil oxidation can be significantly slowed down by the introduction of effective antioxidant additives, purification of base oils from unwanted compounds, and the use of synthetic base components. When the oil is oxidized, its viscosity and corrosiveness increase, its tendency to form deposits, heavy contamination of the filters, which leads to difficult cold start-up and deterioration of oil pumpability. In the engine, oil oxidizes most intensively in thin layers on the surfaces of parts that are heated to high temperatures and come into contact with hot gases. Significant oxidation of oil occurs on pistons, cylinders, piston rings, valves, etc. The speed and degree of oxidation of engine oil significantly increases under the action of products of incomplete combustion of fuel that break into the engine crankcase. Oil oxidation is also accelerated by metal particles that accumulate in it due to wear of engine parts, and organometallic compounds of copper, iron, and other metals that are formed as a result of corrosion of engine parts or the interaction of these parts with organic acids.

With long-term operation of the oil in the engine, as a result of oxidation, a significant increase in viscosity is observed, which occurs after the activation of the antioxidant additive. In the standards for motor oils, their resistance to oxidation is assessed by the induction period of precipitation (oxidation at 200°C according to GOST 21063-77) or the increase in their viscosity during operation in the engine of the ICM installation (motor tests according to GOST 20457-75).

**Anticorrosive properties.** These properties of motor oils depend mainly on the effectiveness of anti-corrosion and antioxidant additives, and even on the composition of the basic components. During the operation of the oil in the engine, its corrosiveness increases. The corrosiveness of oils from low-sulfur oils with a high content of paraffinic hydrocarbons, which in the process of oxidation form aggressive organic acids, increases the most. These acids interact with non-ferrous metals and their alloys.

Anti-corrosion additives protect bearing liners and other parts made of non-ferrous metals, forming a strong protective film on the surface.

**Neutralizing ability** – is the most important chemical property of motor oils, which is characterized by the alkaline number. It shows how many acids formed during oil oxidation or entering it from fuel combustion products can be neutralized by a unit of oil mass. **The alkaline number of oils** is determined by the content of detergents and dispersing additives in them, which have alkaline properties and prevent the deposition of tar-asphalt substances, carbenes and carbides on the parts of the crank-connecting mechanism and especially on the parts of the cylinder-piston group of engines in the form of varnish and soot.

The higher the concentration of the additive in the oil (alkaline number), the less carbon deposits in the engine. However, the concentration of the additive in the oil gradually decreases (activates) during engine operation and the protective properties of the oil deteriorate.

The alkaline number of motor oil is determined by the method of potentiometric titration according to GOST 11362-96 (ISO 6619-88). The alkaline number is taken as the amount of alkali, expressed in milligrams of potassium hydroxide (KOH) per 1 g of sample, required for potentiometric titration of the tested mass in a certain solvent from the initial reading of the measuring device to the reading corresponding to a freshly prepared acidic non-aqueous buffer solution.

**Flash point and ignition temperature.** Engine oils evaporate when heated. Oil vapors, mixing with air, form an explosive mixture.

**The flash point** – is the minimum temperature at which oil vapors, heated in a special device, form a mixture with air that ignites from an external fire source.

**Ignition temperature** – is the temperature of heated oil at which it ignites by itself.

Flash and ignition temperatures characterize the flammability of an oil product. The flash point can be used to evaluate the properties of the hydrocarbons that make up the oil, determining the presence of fuel impurities in it. In the presence of fuel, the flash point of oil is significantly reduced: when 1% of gasoline gets into the oil, it goes from 200 to 170°C, and when there is 6% of gasoline in the oil, it almost doubles.

Flash point is affected by air pressure and humidity. As the atmospheric pressure increases, the flash point slightly increases, and as the air humidity increases, it decreases.

The mixture of oil vapors with air takes place at a certain minimum concentration of vapors in the air, which corresponds to the lower explosive limit.

**Low temperature properties.** These properties are evaluated by viscosity and solidification temperature. **The solidification temperature** – is the temperature when the oil loses its mobility, that is, it stops flowing under the influence of gravity.

The requirements for the quality of motor oils have increased dramatically in connection with the constant improvement of engine designs and the solving of problems related to improving their fuel efficiency (energy saving), reducing consumption and increasing the oil change period (20...50 thousand km for cars). The environmental factor is gaining great importance in connection with the introduction of regulations on the emission of harmful substances with exhaust gases, the gradual rejection of the use of harmful components, for example, aromatic hydrocarbons.

The main directions in ensuring the requirements for the quality of motor oil: increasing the thermo-oxidative stability of oils, reducing low-temperature viscosity, improving cranking and pumping indicators at cold start, creating long-lasting oils and wide use of energy-saving oils.

### 8.3 CONTROL QUESTIONS

1. What is friction? What types of friction do you know?
2. What is the lubricating capacity of oil?
3. What is wear and tear? What types of wear and tear do you know?
4. Name the main functions of motor oil in the engine.
5. List the operational properties of motor oils.
6. Define the viscosity index.
7. What is thermooxidative stability?
8. What is the difference between flash and ignition temperature?
9. What is the freezing point?

## LECTURE 9. MOTOR OILS (part 2)

Lecture plan:

9.1 Base oils.

9.2 Additives to oils.

9.3 Classifications of motor oils.

9.4 Change in the quality of engine oils during engine operation.

9.5 Control questions.

### 9.1 BASE OILS

In the production of motor oils, base oils (liquid lubricants) are used, to which additives are added to obtain marketable products. **Base oils of three types** are used: mineral, synthetic and partially synthetic. **Mineral oils** are obtained in the process of refining oil, **synthetic oils** are obtained through chemical reactions aimed at the formation of identical molecules of organic substances with the desired properties. Partially synthetic (**semi-synthetic**) consist of mixtures of mineral and synthetic base oils.

Since mineral oils cannot always meet the requirements of rapidly developing technology, synthetic oils are increasingly used. The main advantage of synthetic oils over mineral oils is that they can be prepared with predetermined properties depending on specific application conditions. By creating compositions of mineral and synthetic oils with additives or fully synthetic oils, you can get lubricants that meet all the requirements of modern technology. The scope of their application is constantly expanding. Thus, in Germany and France, the share of synthetic oils exceeds 30%. The cost of synthetic oils is approximately 5 times higher than mineral oils, but their service life is longer than that of mineral oils.

Synthetic oils include the following products:

➤ polyalphaolefins are hydrocarbon compounds that do not contain sulfur, phosphorus or metals. Their solidification temperature is below  $-40^{\circ}\text{C}$ , the viscosity index exceeds 140. They have good thermo-oxidative stability;

➤ esters of two basic acids – do not contain sulfur, phosphorus, metals and paraffins. Their solidification temperature is  $-50 \dots -60^{\circ}\text{C}$ . They have good thermo-oxidative stability and high solubility. They are "clean-working", that is, they are more likely to dissolve varnishes and precipitates than to form deposits, and are also able to remove deposits in the engine formed by other oils;

➤ alkylated aromatic additives – have high thermo-oxidative stability and viscosity index, are not prone to the formation of deposits.

Advantages of motor oils on a synthetic basis compared to mineral oils:

✓ lower dependence of viscosity on temperature, i.e. higher viscosity index;  
✓ good low-temperature properties, low solidification temperature and quick flow of oil to lubricated parts, i.e. good pumpability;

✓ low evaporation at high temperature, low oil consumption and low emission of toxic substances by exhaust gases;

✓ high resistance to oxidation, thermo-oxidative stability and low tendency to form deposits;

✓ reliable lubrication of friction surfaces at high loads and temperatures;

✓ long oil life and lower engine maintenance costs.

Disadvantages of synthetic oils:

- increased corrosion in relation to alloys of non-ferrous metals;
- relatively high cost.

## 9.2 ADDITIVES TO OILS

Additives are added to oils to improve their quality. The most important of them are viscous, detergent-dispersing, antioxidant and depressant.

**Viscosity** (thickening) additives are added to motor oils to increase their viscosity and viscosity index. Such oils are called thickened. Thickening additives (the term "viscosity modifiers" is now increasingly used) in combination with additives that improve the lubricating properties of motor oils, make it possible to create energy-saving oils.

Unlike non-thickened oils, the viscosity of which depends mainly on temperature and pressure, thickened oils also have the ability to change their viscosity depending on the stress and shear rate gradient. They reveal a temporary drop in viscosity with increasing shear rate. Such fluids are called "shear-thinned". Examples of such liquids: rubber glue, thickly grated paint, bitumen. The viscosity of these liquids is called imaginary. Its decrease at a certain shear rate gradient is greater, the lower the oil temperature.

In thickened oils, there is also a permanent decrease in viscosity due to mechanical and thermochemical destruction of thickening additives. In the CIS, polymethacrylates are mainly used as commercial viscosity additives. Viscosity additives also include copolymers of styrene with diene hydrocarbons (isoprene or butadiene), copolymers of ethylene with propylene and with higher olefins, esters of mono- and polybasic acids.

Polymethacrylate molecules at low temperature, when the oil is viscous, are in a twisted state and have little effect on viscosity. With increasing temperature, they untwist and increase viscosity (Fig. 9.1). Polymers compensate for the significant loss of oil viscosity when the temperature rises. Thus, the viscosity index of the oil increases.

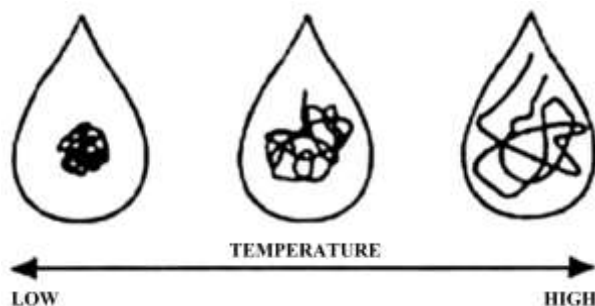
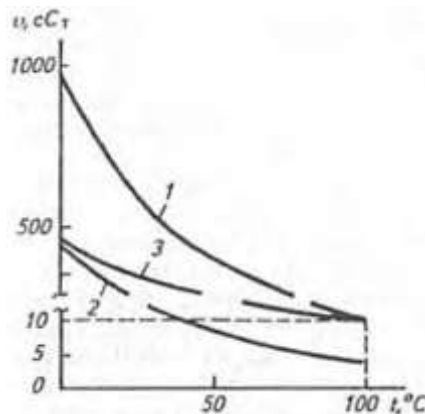


Figure 9.1 – The state of the viscosity additive molecule in the oil at different temperatures

Additives of the polymethacrylate type PMA B-1, PMA B-2, "Diz-acryl" are oil solutions of ethers of methacrylate acid and oils of synthetic fatty alcohols.

Viscosity additives KP-5, KP-10 and KP-20 are products of isobutylene polymerization. The average molecular weight of additives is from 4000 to 25000. They are used in the form of oil solutions in transformer or industrial oil.

The temperature dependence of the viscosity of various oils is shown in Figure 9.2.



1 - motor; 2 - low-viscosity mineral; 3 - thickened motor.

Figure 9.2 – Dependence of oil viscosity on temperature

As can be seen from the figure, when the temperature drops, the viscosity of motor oil increases strongly, and that of low-viscosity mineral oil changes along a gentle curve. By adding to the last viscosity additives, a thickened motor oil is obtained, the viscosity of which at 100°C is increased due to the addition of the additive, and at 0°C it is the same as that of low-viscosity non-thickened mineral oil.

Thickened oils have a high viscosity index, good fluidity at low temperatures, contribute to easy and quick starting of the engine in the cold season, form a small amount of soot, ensure minimal power losses due to friction, which leads to fuel economy.

**Detergent-dispersing additives** are designed to prevent or reduce the formation of varnish deposits and precipitation on working surfaces, prevent burning of piston rings, and also to maintain oil oxidation products in a suspended state. For these purposes, washing (detergents) and dispersing (dispersants) additives are introduced into motor oils. Detergent-dispersing additives are conventionally divided into two groups: ash-based and ash-free.

The molecule of ash additives contains polar groups that are adsorbed on the surfaces of oil oxidation particles, preventing their aggregation and deposition on working surfaces. Thus, the formation of deposits and varnishes on engine parts is prevented. Ash detergent additives of increased alkalinity neutralize acidic products formed as a result of oil oxidation.

In the production of motor oils, domestic detergents of three classes are used: alkylphenolates, sulfonates, and alkylsalicylates of alkaline earth metals. These additives make up the majority of additive compositions in motor oils, but there is a trend towards their decrease due to the increase in the share of ashless dispersants and antioxidant additives.

**Compositions and packages of additives.** Growing requirements for the quality of oils have led to the need to create compositions of multifunctional additives that increase many operational properties of oils. When making compositions, additives are not just mechanically combined, but chemically interact. Therefore, old or new qualities of additives are strengthened.

To simplify storage, transportation and ease of mixing base oils with additives, additive packages are produced, which do not include only viscosity and depressant additives. If necessary, they are added to the oil. By changing the dosage of the additive package, you can prepare oils with different levels of operational properties. Packages of additives usually contain up to 15 components. They are injected into the oil in a concentration of up to 12% (mass fraction).

### 9.3 CLASSIFICATIONS OF MOTOR OILS

Olives have different names and alphanumeric designations. However, if the oil meets strict international standards, i.e. it is of high quality, it is usually classified according to the viscosity class of SAE (Society of Automotive Engineers) and according to operational properties of ARI (American Petroleum Institute) and ASEA (Association of European Automobile Manufacturers).

Oil refineries of our country use these classifications when labeling oils.

#### *Classification of motor oils by viscosity according to SAE.*

This classification is practically accepted in many countries. Its latest version is presented in table 9.1.

Table 9.1 – Classification of SAE J300

Class for SAE	Low temperature viscosity		High temperature viscosity		
	Scrolling *	Pumping **	Viscosity***, mm <sup>2</sup> /s, at 100°C		Viscosity**** MPa·s, at 150°C and shear rate 106 s <sup>-1</sup> , not less
	Maximum viscosity, MPa·s, at temperature, °C	Maximum viscosity, MPa·s, at temperature, °C	Min	Max	
0W	3250 at -30°C	60000 at -40°C	3,8	–	–
5W	3500 at -25°C	60000 at -35°C	3,8		
10W	3500 at -20°C	60000 at -30°C	4,1	–	–
15W	3500 at -15°C	60000 at -25°C	5,6	–	–
20W	4500 at -10°C	60000 at -20°C	5,6	–	–
25W	6000 at -5°C	60000 at -15°C	9,3	–	–
20	–	–	5,6	< 9,3	2,6
30	–	–	9,3	< 12,5	2,9
40	–	–	12,5	< 16,3	2,9*a
40	–	–	12,5	< 16,3	3,7*b
50	–	–	16,3	< 21,9	3,7
60	–	–	21,9	< 26,1	3,7

\* Viscosity is measured by the ASTM D 5293 method on a CCS viscometer.

\*\* Viscosity is measured according to the ASTM D 4684 method on an MRV viscometer; shear stress is not allowed for any viscosity value.

\*\*\* Viscosity is measured by the ASTM D 445 method on a capillary viscometer.

\*\*\*\* Viscosity is measured by ASTM D 4683 or SES L-36-A-90 on a tapered bearing simulator.

\*a This value is for SAE classes 0W-40, 5W-40, 10W-40.

\*b This value is for classes SAE 40, 15W-40, 20W-40, 25W-40.

According to this classification, oils are divided by viscosity characteristics into 11 classes, six of which are winter (SAE 0W, 5W, 10W, 15W, 20W and 25W). Here the letter W means "Winter" – winter. A thickening additive is added to winter grade oils. Five classes refer to summer oils (SAE 20, 30, 40, 50, 60).

A common feature for motor oils of all classes is the kinematic viscosity at 100°C. For *winter oils*, only the minimum value of kinematic viscosity is normalized, and for *summer oils* – wide limits of kinematic viscosity at 100°C of each class.

*An all-season olive* is called an olive that corresponds to one of the winter classes in terms of low-temperature dynamic viscosity, and one of the summer classes in terms of kinematic viscosity at 100°C and dynamic viscosity at 150°C. In the designation of all-

season oils, one of the winter classes is indicated first, and then one of the summer ones. For example, SAE 5W-40, SAE 10W-30, other.

Table 9.1 *for summer classes* of motor oils shows the minimum values of dynamic viscosity at a temperature of 150°C and a shear rate of 106s<sup>-1</sup>. These conditions are characteristic of the oil film in the main and connecting rod bearings of the crankshaft and between the cylinder and the piston ring in a warmed-up engine in the summer.

*For winter classes*, two values of the maximum permissible dynamic viscosity are set, at which it is possible to start the engine cold without preheating (turning) and satisfactory pumping of engine oil by the pump through the lubrication system when the engine crankshaft is turned by the electric starter.

The low-temperature viscosity of engine oil (turning and pumping) in table 9.1 is given in dynamic viscosity units. To determine this viscosity, rotary viscometers are used, in which the moment of resistance of the rotating shaft serves as an indicator of the resistance to the flow of liquid. Rotary viscometers include a cold start simulator and a mini-rotary viscometer. The shear speed in them can be varied by changing the dimensions of the rotor, the gap between the walls of the rotor and the stator, and the speed of rotation. With the help of a cold start simulator, reliable results are obtained, corresponding to the cold rotation of the engine shaft. The mini-rotational viscometer provides a low shear rate during measurement. It measures the critical shear stress at which fluid flow begins. Oil pumping is determined on this viscometer.

In order to guarantee the pumping of engine oil during a cold start of the engine, the norms of maximum dynamic viscosity for winter classes are set 5°C below the viscosity norms, which guarantee the turning of the engine by the electric starter with a sufficient rotation frequency for starting. In this way, oil supply by the pump is ensured at a cold start and a sufficient speed of filling the funnel, which is formed on the surface of the oil in the crankcase under the oil pick-up. It should be noted that there is no unequivocal relationship between the freezing point of the oil and the limit temperature of the cold start of the engine.

#### ***API classification of motor oils.***

The first classification of motor oils according to conditions of use and levels of operational properties was proposed by the American Petroleum Institute (API) back in 1947. Since then, it has been changed and supplemented many times, but the principle of dividing motor oils into two categories has always been preserved (Table 9.2).

***Category "S" (Service)*** includes oils intended for 4-stroke gasoline engines of passenger cars, minibuses, and pickup trucks.

***Category "C" (Commercial)*** includes oils intended for diesel vehicles, road construction equipment and agricultural machines.

Oils that can be used to lubricate gasoline and diesel engines are called ***universal***.

The levels of operational properties according to API, in order of their growth, are indicated by the first letters of the Latin alphabet, standing behind the letters "S" or "C", which indicate the field of application. So far, nine classes (SA, SB, SC, SE, SF, SG, SH, SJ) have been introduced into the Service category, and ten classes into the Commercial category (CA, CB, CC, CD, CD-II, CE, CF, CF-2, CG-4).

The numbers in the designations of classes CD-II, CF-2, CG-4 give additional information about the use of oils of this class in 2-stroke or 4-stroke diesel engines, respectively. Double labeling is used to designate universal oils, for example, CF-4/SG, SH/CG-4, other.

Table 9.2 – Modern classification of motor oils according to API

API category and class	Area and conditions of application
	<b>Category Service</b>
SH	Oils intended for gasoline engines of cars manufactured in 1994 and earlier replace SG class oils.
SJ	The same, but with the introduction of additional requirements for oil consumption in the engine, energy-saving properties (fuel economy) and the ability to withstand heat without forming deposits.
	<b>Category Commercial</b>
CF	Oils intended for off-road diesels with a split combustion chamber and running on fuel with a high sulfur content (up to 0.5%).
CF-4	Oils intended for 4-stroke diesel engines of trucks carrying out transportation on highways. They have better cleaning properties than CE class oils and can replace them in diesel engines manufactured before 1990.
CR-2	Oils intended for 2-stroke diesel vehicles; replace CD-II class oils, as they have better cleaning and anti-wear properties.
CG-4	Oils intended for 4-stroke diesel engines, off-road vehicles and trucks that comply with toxic emissions standards established in the USA since 1994. Compared to CF-4 class oils, they have better cleaning, anti-wear, anti-corrosion properties, less foaming at high temperature and are well combined with low-sulfur diesel fuels (sulfur content less than 0.05%). CF-4 oils are replaced in previously released engines.

Obsolete classes are excluded from the API classification due to unnecessaryness. Today, in the USA, only oils with higher levels of operational properties are certified, namely: SH and SJ for gasoline engines, CF, CF-2, CF-4 and CG-4 for diesel engines.

**Perspectives.** Class RS-9 (project) is being developed in connection with new environmental requirements formulated by the American Environmental Protection Agency. To ensure these requirements, it is necessary to create a system of recirculation of exhaust gases. For this, the design of the engines should be changed and motor oils should be given new operational properties. At the same time, it is expected to increase the specific power of the engines.

The main features of oil operation in conditions of exhaust gas recirculation and increased specific power are increased oil acidity, soot formation and, in connection with this, an increase in oil viscosity, significant wear of engine parts and a higher operating temperature of the engine and oil.

API EC category - energy-saving low-viscosity oils (Energy Consenting), which reduce fuel consumption according to the results of tests on gasoline engines.

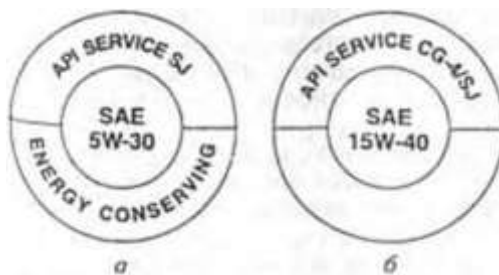
**Classes of olives.** SH/EC (obsolete) - gasoline savings of at least 1.5% compared to the SAE 20W-30 reference oil;

SH/EC II (obsolete) – fuel savings of at least 2.7% compared to the SAE 20W-30 reference oil;

ARI SJ/EC (current) – savings depending on the viscosity of the oil being tested.

Universal oils for gasoline and diesel engines are indicated by two symbols of the corresponding categories: the first symbol is the main one, and the second indicates the possibility of using the oil for another type of engine. For example, API SH/CF-4 is an oil for use mainly in gasoline engines, but it can also be used in diesel engines for which the class CF-4 and below is offered (CF, CE, other.).

**API mark.** For motor oils that meet the requirements of the current quality categories and have passed the official API – SAE tests, the "API service symbol" mark is placed on the labels. This sign indicates the viscosity and operational properties of the oil and the possible degree of energy saving (Fig. 9.3).



*a - high-quality energy-saving oils; b - for high quality oils.*

Figure 9.3 – "API service symbol" signs

The newest categories of API-certified oils are marked with the symbol "API Certification Certificate", the so-called "Starburst" sign (Fig. 9.4). These oils must meet the requirements of ILSAC (International Lubricants Standardization and Approval Committee). The sign is assigned only to energy-saving oils of the highest quality with viscosity SAE 0W-..., 5W-... and 10W.



Figure 9.4 – API certification mark "Starburst"

An example of the SAE and API brand designation of motor oil: Castrol SAE 5W-30, API SJ/CF-4, EC. The first words and brands usually indicate the name of the company. Universal all-season oil. The low-temperature viscosity corresponds to class 5W (dynamic viscosity – rolling 6600 mPa at -30°C, pumping 60000 mPa at -35°C). High-temperature kinematic viscosity corresponds to class 30 (min 9.3, max 12.5 mm<sup>2</sup>/s). High-temperature dynamic viscosity at a shear rate of 10<sup>6</sup>s<sup>-1</sup> is not less than 2.9 mPa·s. The oil is mainly used in gasoline engines of passenger cars (class SJ), but it can also be used in diesel engines of passenger cars (class CF-4). It has energy-saving properties (ES).

Approximate correspondence of viscosity classes according to GOST 17479.1–85 and SAE is given in table 9.3.

Table 9.3 – Correspondence of viscosity classes and groups of motor oils according to GOST 17479.1-85 to SAE and API classifications

Viscosity class		Viscosity class	
GOST 17479.1-85	SAE	GOST 17479.1-85	SAE
3 <sub>3</sub>	5W	24	60
4 <sub>3</sub>	10W	3 <sub>3</sub> /8	5W-20
5 <sub>3</sub>	15W	4 <sub>3</sub> /6	10W-20
6 <sub>3</sub>	20W	4 <sub>3</sub> /8	10W-20
6	20	4 <sub>3</sub> /10	10W-30
8	20	5 <sub>3</sub> /10	15W-30
10	30	5 <sub>3</sub> /12	15W-30
12	30	6 <sub>3</sub> /10	20W-30
14	40	6 <sub>3</sub> /14	20W-40
16	40	6 <sub>3</sub> /16	20W-40
20	50		
GOST 17479.1-85	API	GOST 17479.1-85	API
A	SB	Г <sub>2</sub>	CC
Б	SC/CA	Д <sub>1</sub>	CF
Б <sub>1</sub>	SC	Д <sub>2</sub>	CD
Б <sub>2</sub>	CA	Е <sub>1</sub>	SG
B	SD/CB	Е <sub>2</sub>	CF-4
Б <sub>1</sub>	SD		SH*
Б <sub>2</sub>	CB		SJ*
Г	SE/CC		CG-4*
Г <sub>1</sub>	SE		

\* These API classes have no analogues in the domestic classification.

These classes have only the characteristics of kinematic viscosity at 100°C. The low-temperature characteristic according to GOST 17479.1-85 is established at a temperature of -18°C by kinematic viscosity, which is determined by extrapolation. Determination of dynamic viscosity at 150°C and high shear rate is not provided by this standard.

A reduction in viscosity (to SAE 10W or SAE 5W) provides an average fuel saving of 1...2%. The use of high-quality synthetic motor oil of the SAE 0W-40 class allows you to reduce fuel consumption by 6% compared to standard mineral oil.

The US and Japanese automotive companies have developed uniform minimum requirements for motor oils for automobile engines in the ILSAC classification, which contains two classes of oils, designated GF-1 and GF-2. They are practically identical to oils of classes SH and SJ according to API. These oils have high energy-saving properties, are all-season; the winter characteristic is limited to the least viscous SAE 0W, 5W and 10W oils, and the summer class can be any. API certifies motor oils for compliance with ILSAC classes. At the same time, they are marked with a standard symbol (a quality mark in the form of a gear with the text in English inside the picture: "American Petroleum Institute. For gasoline engines. Certified").

Automobile manufacturers of European countries developed and introduced their classification of ACEA (Association of European Manufacturers) motor oils in 1996. This classification in terms of requirements for motor oils differs significantly from the American API, which is due to the peculiarities of operating conditions and constructive solutions in the automotive industry in the USA and Western European countries.

### ***Classification of motor oils ACEA.***

This classification has been in effect since 1996, replacing the RSMS (Committee of General Market Automobile Manufacturers). The requirements of the European standards for the quality of oils are stricter than the American ones, because in Europe the operating conditions and the design of the engines are significantly different from the American ones. Engines produced in Europe are characterized by a higher degree of forcing, maximum crankshaft rotation frequency, lower mass and higher specific power. Vehicles with such an engine have high permissible speeds, and city modes are more difficult for them.

There are three categories of motor oils in the ASEAN classification: A – for gasoline engines; B – for low-power diesel engines installed on cars and trucks of small capacity; E – for powerful diesel engines.

Each category consists of several classes. The quality level and purpose of the oils of each class are indicated by numbers. In addition, the year of approval of the class is indicated. For example, ASEA AZ-98, ASEA E5-99.

Classes of category A: A1-96, A1-98, A2-96, AZ-96, AZ-98.

Classes of category B: B1-96, B1-98, B2-96, B2-98, VZ-96, VZ-98, B4-98.

Classes of category E: E1-96, E2-96, EZ-96, E4-99, E5-99.

Class A1-98 – oils for passenger car engines, allowing the use of oils with low high-temperature viscosity (2.9...3.5 mPa·s) in conditions of high shear speeds, which significantly reduces fuel consumption. Oils have quite high anti-wear properties.

Class A3-98 – is a universal oil with very high operational properties for powerful gasoline engines. Extended replacement intervals, year-round use and use in severe operating conditions are allowed.

Class A5-01 – this class meets the highest requirements for oils for gasoline engines of modern and promising passenger cars.

Class B1-98 – oils for diesel engines, which allow the use of oils with low high-temperature viscosity (2.9...3.5 mPa·s) at high shear speeds, thanks to which great fuel economy is achieved. Oils have good anti-wear properties.

Class B2-98 – is a universal oil that can be used in most diesel engines of passenger cars at normal oil change intervals. Not recommended for high pressure engines.

Class B3-98 – oils with high operational properties for high-pressure diesel engines of passenger cars. Extended replacement intervals, year-round use and use in severe operating conditions are allowed.

Class B4-98 – universal oils for diesel engines with direct fuel injection of passenger cars and vans. It has high operational properties.

Class E4-99 – is a very high-quality oil for powerful and fast-moving Euro1, Euro2, Euro3 diesel engines. Oils have increased replacement intervals.

Class E5-99 – is the most perfect oil, unmatched in quality, for Euro1, Euro2, Euro3 diesel engines. Oils have high stability, a long service life, keep the engine clean and prevent engine parts from wearing out. They meet the high requirements of European and American car manufacturers.

The "approval" of car manufacturers is indicated in the labeling of motor oils. It is represented by a trademark or code and means that the use of this oil is approved by the cars of this manufacturer. On containers with motor oils, the classification is usually indicated: SAE, API or ACEA.

Example of motor oil marking: SAE 5W-50, API SJ/CF, ASEA A3-98/V3-98,

VW 501.01/505.00, MB 229.1, BMW, Porsche, viscosity-temperature properties are marked SAE 5W-50 (all-season oil, which contains the properties of winter SAE 5W and summer SAE 50 oil classes). Operational properties according to the classification of API and European ASEA, API SJ/CF means that the oil is intended for gasoline engines (SJ), but can also be used for diesel engines (CF). ASEAN A3-98; V3-98/A3-98 – high-class oil for gasoline engines with and without supercharging of modern European cars; VZ-98 is a high-class oil for supercharged diesel engines of modern European cars.

In the indicated brand, the manufacturers' approval means the following:

VW – Volkswagen-Audi, 501.01 – all-season oil; 505.00 – for turbocharged engines;

MB – Mercedes-Benz, 229.1 – oil for passenger car engines produced since 1997;

BMW, Porsche are company names.

A canister with semi-synthetic oils is usually labeled Semi Synthetic, and fully synthetic oils are labeled Fully Synthetic.

#### **9.4 CHANGE IN THE QUALITY OF MOTOR OILS DURING ENGINE OPERATION**

In connection with the increase in power, the change in design and the complication of operation of modern engines, the working conditions of oils have become stricter. However, oil change times are continuously increasing due to improvements in their quality. Premature replacement of oils is economically impractical, as their consumption, maintenance costs, spare parts, etc., increase. An unjustified increase in the service life of oils leads to increased wear of engine parts, which reduces the reliability of the engine and increases its failures. Determining the optimal frequency of oil change is a time-consuming and long-term work, which has an important economic and technical significance.

Periodic addition of oil during operation partially restores the initial properties of oils. After a certain time, the oil must be completely replaced. The periodicity of changing the oil depends on its properties, the type of engine, its technical condition and operating conditions, the technical condition of the oil system, the method of filtration, fuel, the professionalism of the driver and other factors. The need for a complete replacement is due to the loss of the main operational qualities of the oil, that is, its aging. The main reason for the activation (aging) of the oil is the oxidation of the oil and the activation of additives. In addition, the oil is contaminated with solid products of its oxidation, carbon particles, dust, sand that get into the oil from the outside, metal particles formed as a result of wear of engine parts, and metal corrosion products, unburned fuel, sulfur compounds contained in spent gases, water formed during condensation from exhaust gases and entering from the outside with air, as well as evaporation of light fractions of oil.

Oil contamination occurs during its transportation, storage and refueling. The amount of mechanical impurities in the oil can be 0.2%. Impurities entering from the outside and formed during oil operation change the nature of friction, clog oil filters and channels, increase the operating temperature of engine parts, and cause their increased wear.

Oil contamination with impurities is caused by an increase in gas breakthrough into the oil sump, and even by products of incomplete fuel combustion. The increased content of mechanical impurities in the oil indicates a poor technical condition of the filtration system. As a result of the use of a full-flow system of fine cleaning of engine oil, the wear of the main parts of the engine is reduced by two to three times and the service life of the engine oil is significantly increased.

Modern engines are characterized by a reduced volume of the oil system, as a result of which the productivity of oil pumps and the multiplicity of oil circulation are increased. The latter increases the saturation of the oil with air, which, in turn, leads to an increase in the rate of its oxidation and increased wear of engine parts.

Along with operation in forced modes, many cars are characterized by engine operation with frequent stops, long idling. In urban conditions, engines operate at partial loads about 80% of the time. In this mode, engines operate at low temperatures, especially in winter. For example, in urban conditions with an ambient air temperature of  $-10...-15^{\circ}\text{C}$  and a trip of up to 20 km, the temperature of the liquid in the cooling system is about  $50^{\circ}\text{C}$ . At reduced thermal modes of engine operation, the rate of formation of low-temperature precipitation, oil contamination due to incomplete combustion of fuel and increased condensation of water vapor increases. Long-term operation of the engine at reduced speeds leads to contamination of pistons, rings and increased oil consumption due to an increase in its smoke.

The relative oil consumption, depending on the condition of the oil rings and engine wear, is approximately as follows:

new engine, after running in – 100%

new engine one with clogged slots of oil-receiving rings – 460%

worn out engine – 722%

worn out engine with clogged slots of oil-receiving rings – 4400%

The type and composition of fuel significantly affect the formation of carbon and other deposits on diesel engine parts. Yes, the exhaust gases of diesel engines contain a significant amount of soot. The amount of soot that gets into the oil, for example, in an engine of the YaMZ-238 type for 200 hours of operation can be from 60 to 600 g. The worse the technical condition of the engine, the more soot is contained in the exhaust gases and the more it gets into the oil. The composition and amount of deposits on engine parts leads to serious disturbances in its operation and can be the cause of failure.

The effect of fuel on the amount of organic deposits in the oil is sharply reduced during the operation of the engine on gaseous fuel. So, impurities in the oil of diesel engines are 5 times more than in gasoline engines, and 10...20 times more than in the oil of engines running on gaseous fuel. According to NAMI, after 10,000 km of mileage, there are significantly fewer impurities in the oil of an engine running on gaseous fuel than after 5,000 km of the same vehicle running on gasoline; in the oil of a truck running on gaseous fuel, after 5 thousand km the amount of impurities was 0.07%, after 10 thousand km – 0.11%, and in the oil of a truck running on gasoline, the content of impurities after 5 thousand km mileage was 0.4%.

Aging of oil leads to coking of piston rings, their burning, loss of mobility; an increase in the temperature of parts of the cylinder-piston group due to the deterioration of heat dissipation; jamming of valves in guide bushings; valve burnout; reduction of the cross-section of the intake and exhaust tracts; contamination of the nets of oil receivers of pumps, filters, oil channels of the lubrication system, drainage holes in oil rings and pistons; changes in oil viscosity; increased corrosive wear of parts of the cylinder-piston group; abrasive wear of parts with solid particles of impurities; corrosion of bearing alloys and rusting of iron-containing parts.

Filter elements and crankcase ventilation slow down, but do not prevent, oil aging.

The periodicity of oil replacement is established on the basis of a thorough study of

its operational properties and their changes during operation. Modern car fleets use high-quality new oils. However, the accepted periodicity of oil replacement is still insufficiently substantiated, since the experience of operating new equipment is only partially taken into account. Therefore, it is necessary to adjust the replacement terms set by the manufacturer, after sufficient accumulation and study of the results of operation.

It is not yet possible to determine the timing of oil replacement based on their color change. For example, the oil turns black after several tens of hours of work due to the accumulation of additives. However, despite the black color, it still has high operational quality indicators.

Some of the defective indicators of used oils are listed in Table 9.4.

Table 9.4 – Defective indicators of used oils

Indicator	The value of oil indicators for engines	
	gasoline	diesel
Viscosity change, %:		
increase	25	40
decrease	20	30
The content of impurities insoluble in gasoline, %, is slightly higher	1,0	3,0
Water content, %, slightly more	0,3	0,3
Fuel content, %, no more	0,8	0,8
Alkaline number, mg KOH/g, at least	0,5...2*	1...3*
Reduction of the flash point, °C, no more	20	20

\* Higher values for oils of higher groups.

Methods such as determining the content of wear products and determining alkalinity are not suitable for daily quality control of working oil, although these analyzes are the most reasonable and reliable for determining the operability of oils.

The service life of the oil is established based on economic and technical feasibility. The service life of oils in engines running on gaseous fuel is 2 times longer than in engines running on liquid fuel. The service life of engine oil is reduced by 1.5...2 times for engines running on leaded gasoline compared to the service life of the oil in an engine running on regular gasoline.

The periodicity of oil change is established by the vehicle manufacturer, indicating it in maintenance maps and tables. To increase the service life of the oil, it is necessary to flush the system when replacing it.

The specialists of the "Kvalitet" NVP have developed a self-regulating engine lubrication system, which provides a significant extension of the engine oil's service life and increases its efficiency during operation. The system consists of high-speed ( $n=10,000...12,000 \text{ min}^{-1}$ ) centrifugal filters – supercentrifuges and a device that maintains the stability of the physico-chemical properties of the oil. This device injects a new portion of the additive into the oil as it is activated. A self-regulating lubrication system is the first step to operating engines without changing engine oil.

## **9.5 CONTROL QUESTIONS**

1. List the requirements for the operational properties of motor oils.
2. Why are additives added to motor oils?
3. How are motor oils classified according to operational properties?
4. How are motor oils classified by viscosity?
5. Name the main advantage of synthetic oils over mineral oils.
6. Which olive is called all-season thickened?
7. How are motor oils labeled?
8. What motor oils are used for gasoline engines?
9. What motor oils are used in diesel engines?

## LECTURE 10. TRANSMISSION OILS

Lecture plan:

10.1 Introduction.

10.2 Basic operational properties of transmission oils.

10.3 Classification of oils according to operational properties and purpose.

10.4 Change in the quality of transmission oils during operation.

10.5 Control questions.

### 10.1 INTRODUCTION

Transmission and gear oils are used in most modern machines and mechanisms and serve to lubricate various types of gears, pinion gears (cylindrical, hypoid, worm, etc.), and are also a hydraulic working body during power transmission in hydrodynamic gearboxes.

The working temperature of the oil in the transmission units of transport vehicles and industrial gearboxes varies widely: from the temperature of the surrounding air at the time of starting work to 120...130°C and even 150°C.

The minimum oil temperature in car transmission units in a cold zone can reach -60°C, in a temperate zone up to -40°C, and in a hot zone up to -10°C.

The sliding speed (for different types of gears from 1.5 to 25 m/s) and the specific loads on the surface of the gear teeth (from 0.5 to 2 GPa in the engagement pole, and in hypoid gears up to 4 GPa) largely determine the type of oil, which is used in gear transmission. When the load increases, the lubricating film that separates the rubbing surfaces can begin to break down, which will lead to direct contact of metal surfaces, their sticking and catastrophic wear. As the sliding speed increases, the temperature at which seizing begins decreases, and the conditions for catastrophic wear appear.

*Transmission oils* can be divided into the following types according to *the level* of tension of the gears:

- *universal*, ensuring the operation of all types of gears and other parts of transmission units that rub;
- *general purpose*, used in cylindrical, bevel and worm gears of cars;
- *oils for hypoid gears* of trucks and cars.

To ensure the reliable operation of modern equipment, transmission and gear oils must meet the following *basic requirements*:

- have a sufficient level of anti-wear and anti-scratch properties;
- have good viscosity-temperature properties;
- do not have a corrosive effect on the parts of the transmission;
- have good thermo-oxidative stability;
- have good protective properties;
- be non-toxic and have good compatibility with stuffing box materials.

### 10.2 MAIN OPERATIONAL PROPERTIES OF TRANSMISSION OILS

*The lubricating properties* of transmission oils depend on their component composition and the amount of anti-friction, anti-wear and anti-seize additives used. The composition of the oil depends on the method of its production, that is, on what the low-viscosity oil is combined with: with residual oils or with an extract (smolka) obtained after

selective purification of oils.

***Lubricating properties of transmission oils should ensure long-lasting and reliable operation of transmission units at high loads and speeds of movement of rubbing surfaces, reducing the intensity of their wear and preventing seizing*** (by forming thin films on them that isolate parts and prevent welding and seizing of teeth).

To improve the lubricating properties of oils, organic substances (sulfur, phosphorus, nitrogen-containing compounds) and organometallic compounds (lead, zinc, aluminum, etc.) are used as additives, which form protective films on the surface of metals.

***Viscosity-temperature properties*** of transmission oils have a great influence on the efficiency of transmission units, ensure the continuity of the flow of oil to the engagement zone of the gear teeth and to the rolling bodies, bearings, as well as the ability of the car to move from its place at low ambient temperatures.

The viscosity level of transmission oil determines the formation of an oil wedge in the area of highly loaded contacts of rubbing parts. The lower level of viscosity of the transmission oil with anti-seize additives is determined by the reliability of the seals of the crankcases of the transmission units. If the seals and other seals are in good condition, the minimum permissible kinematic viscosity of the oil can be 5 mm<sup>2</sup>/s.

The maximum permissible kinematic viscosity of the oil at the lowest operating temperature is 300...600 Pa·s - this is the viscosity at which it is still possible to move the car without heating the oil in the units.

Characteristics of viscosity classes of transmission oils are given in table 10.1.

Table 10.1 – Viscosity classes of transmission oils (GOST 17479.2-85)

<b>Viscosity class</b>	<b>Kinematic viscosity at 100°C, mm<sup>2</sup>/s</b>	<b>The temperature at which the dynamic viscosity does not exceed 150 Pa·s, °C</b>
9	6,00...10,99	-45
12	11,00...13,99	-35
18	14,00...24,99	-18
34	25,00...41,00	–

### **10.3 CLASSIFICATION OF OILS BY OPERATIONAL PROPERTIES AND PURPOSE**

According to the API classification, transmission oils are divided into categories depending on the structural features of transmissions, their operating conditions and the content of additives. Table 10.2 shows the API classification of transmission oils by operating conditions and areas of application and the correspondence of domestic groups of transmission oils to it.

The designation of transmission oils in accordance with GOST 17479.2-85 includes the letters TM, numbers characterizing belonging to the group of oils according to operational properties, and numbers indicating the class of kinematic viscosity (at a temperature of 100°C).

For example, TM-5-93 is a transmission oil of the 5th group, that is, with multifunctional and anti-seize additives of high efficiency, 9th viscosity class, thickened.

Table 10.2 – Correspondence of domestic groups of transmission oils to API classification

Oil group		Field of application
According to GOST 17479.2-85	According to API	
TM-1	GL-1	Mechanisms that require oils with depressant and antifoam additives
TM-2	GL-2	Mechanisms that require oils with antifriction additives
TM-3	GL-3	Drive axles with spiral-bevel gears, requiring the use of oils with weak anti-seize additives
TM-4	GL-4	Hypoid transmissions, requiring the use of oils with anti-caking additives of medium activity
TM-5	GL-5	Hypoid transmissions of trucks and cars, requiring the use of oils with active anti-seize and anti-wear additives
–	GL-6	Hypoid gears operating in very difficult conditions and requiring the use of oils with highly effective anti-seize and anti-wear additives

The TM-1 group includes nigrols – oils for industrial equipment, produced according to TU 38.101.529-75. These oils are also used in transmission units of some tractors, agricultural and road construction machines, planetary gears of lifting cranes and excavators. Nigrols are crude residues of direct oil distillation and are characterized by a high content of resins, asphaltenes, and mechanical impurities. The operational properties of nigrols are low, which limits the scope of their application.

To the same group belong tractor oil AK-15 (TU 38.001280-76), which is currently used very limited, and oil TS-14.5 (TU 38.101.110-71) for lightly loaded transmission units of some cars and tractors, obtained by mixing residual oil and distillate oil of selective purification with the addition of a depressant additive.

The TM-2 group includes TSp-10-EFO oil (TU 38.101701-77), which is a mixture of deasphalt and low-set distillate oil, to which anti-wear and depressant additives are added. The same group includes TEp-15 oil and oil for gearboxes and steering control of vehicles (TU 38.1011332-90).

The TM-3 group includes TSp-10 oil (TU 38.401809-90), as well as TAP-15B and TSp-15K oils, produced according to GOST 23652-79.

The TM-4 group includes oil TSp-15 (GOST 23652-79), and oils TS3-9hip (TU 38.1011238-89) and TShip (TU 38.1011332-90) for hypoid gears.

The TM-5 group includes oils TM5-12(rk) (TU 38.101844-80) and TAD-17 (GOST 23652-79).

Table 10.3 shows the compatibility of brands of domestic and foreign transmission oils.

Table 10.3 – Correspondence of brands of domestic and foreign transmission oils

Domestic oil	Foreign oil	
Brand, standard	Classification	Company, brand
TEp-15 (TM-2-18) GOST 23652-79	API GL-1	Shell, Dentax 90, Mobil, Mobilube C90
TSp-10 (TM-3-9) GOST 23652-79	API GL-3	Shell, Spirax EP 80W, BP, Gear Oil 80EP
TSp-15k (TM-3-18) GOST 23652-79	API GL-3	Shell, Spirax EP 90W, Mobil, Mobilube CX90
TAp-15v (TM-3-18) GOST 23652-79	API GL-3	BP, Gear Oil GP90, Caltex, Thuban 90
TSz-9hep (TM-4-9z) OST 101158-78	API GL-4	Shell, Spirax EP 75W, BP, Gear Oil 75W EP
TAD-17e (TM-5-18) GOST 23652-79	API GL-5	Shell, Spirax ND 90, Mobil, Mobilube ND 90

Table 10.4 gives the SAE J306 classification of transmission oils by viscosity.

Table 10.4 – Classification of transmission oils by viscosity (SAE J306)

Viscosity class according to SAE	The maximum temperature for viscosity is 150,000 sPz, °C	Kinematic viscosity at 100°C, mm <sup>2</sup> /s (cSt)	
		minimal	maximum
70W	-55	4,1	
75W	-40	4,1	—
80W	-26	7	—
85W	-12	11	—
80	—	7	< 11
85	—	11	< 13,5
90	—	13,5	< 24
140	—	24	< 41
250	—	41	—

*The viscosity of the oil should be chosen* taking into account the maximum and minimum temperature of use of the equipment. Therefore, the SAE standard applies only to transmission oil viscosity values measured at high and low temperatures.

Oils of viscosity classes SAE 70W...85W are intended for operation in winter; classes SAE 80...250 – in the summer.

Transmission oils that simultaneously meet high and low temperature requirements are *called all-season*. They are most often used in technology. For example, SAE 80W-90 class oil for the medium climate zone meets the low-temperature requirements for SAE 80W oil (that is, at a temperature of -26°C, the dynamic viscosity of the oil does not exceed 150,000 cPz) and the high-temperature requirements for SAE 90 oil (that is, at 100° the viscosity is in within 13.5 ... 24 cSt).

Examples of the designation of SAE and API transmission oils:

Norsey SAE 85W-90, API GL-5, where Norsey is the name of the company, 85W is viscosity at low temperature, 90 is viscosity at 100°C, GL is gear lubricant, 5 is an oil group.

Taybol SAE 10W-30, API CD/SF, GL-4 is a universal oil used in engines (mainly diesel engines), transmissions and hydraulic systems.

#### **10.4 CHANGE IN THE QUALITY OF TRANSMISSION OILS DURING OPERATION**

Transmission oils are replaced when there is a significant change in their quality indicators. *The operating conditions* of a specific transmission design are *the main factor* that determines the oil change period. Operating conditions mean transmission load, temperature regime, intensity of oil contamination with dust, water and wear products of parts. Quartz dust sharply reduces the anti-wear properties of the oil, which cannot be compensated (improved) by the most effective additives. When water gets into the oil, wear increases by 2 times.

*The oil should be changed when the viscosity increases by 50%.* A necessary condition for the long-term operation of the oil is reliable sealing of the transmission.

The average statistical intervals of changes in domestic oils are:

- *for automatic gearboxes of passenger cars*, as well as gearboxes and other units of truck transmissions *30...50 thousand km*;

- *for gearboxes and other units of transmissions* of mobile machinery in heavy duty modes of *15...30 thousand km*.

#### **10.5 CONTROL QUESTIONS**

1. Under what conditions do transmission oils work?
2. What are the operational requirements for them?
3. How are transmission oils classified by viscosity?
4. Tell us about the groups of transmission oils classified according to operational properties.
5. What oils are used in tractor transmissions?
6. What oils are used in truck transmissions?

## LECTURE 11. OILS FOR VARIOUS PURPOSES

Lecture plan:

11.1 Oils for hydromechanical transmissions of cars.

11.2 Oils for hydraulic systems.

11.3 Oils for technological purpose.

11.4 Control questions.

### 11.1 OILS FOR HYDROMECHANICAL TRANSMISSIONS OF CARS

Since the hydromechanical transmission (HMT) includes several different components - a torque converter, a gear box, a complex automatic control system - more stringent requirements are imposed on the oil working in the HMT than on the oil for conventional mechanical transmissions gears. Due to the lack of a rigid connection between the engine and the transmission, the maximum dynamic loads on the transmission in these cars are lower (according to the test results - by 1.5-3 times).

In HMT, oil performs various functions. Let's consider the main ones:

- ✓ the power developed by the engine is transmitted by the oil to the mechanical gearbox;
- ✓ oil acts as the working fluid of the automatic control system and lubricates hydraulic transmission units;
- ✓ in friction clutches and brakes, oil is also a working medium;
- ✓ in the hydraulic transmission system, oil acts as a cooling medium.

Features of the design, as well as the presence in the HMT of aggregates different in terms of device and operating conditions, impose strict, sometimes contradictory requirements on the oil (for example, increased density and low viscosity, low viscosity and high anti-wear properties, high anti-wear properties and high friction properties).

The average temperature of the oil in the crankcase of the HMT is 80...95°C, and in the summer period during the urban traffic cycle - up to 150°C. This gives reason to consider the HMT as the most thermally stressed of all car transmission units. Unlike a mechanical box, the temperature of the oil in the HMT increases mainly due to internal friction (the speed of the oil flow in the torque converter is significant – 80...100 m/s). In addition, the design of the HMT is such that if more power is removed from the engine than is necessary to overcome road resistance, the excess power is wasted on the internal friction of the oil, which further increases its temperature. The creation of high-speed flows of oil movement in the hydrotransformer leads to intensive aeration, increased foaming, which creates conditions for increased oil oxidation.

**Oil viscosity for HMT** is one of its most important performance indicators. Oil viscosity requirements are determined by the desire to achieve the greatest efficiency of the torque converter, as well as to ensure reliable operation of lubricated parts.

**To ensure the operation of the torque converter with a higher efficiency, the oil should be the least viscous.** Thus, an increase in oil viscosity due to a decrease in its temperature from 90°C to 30°C leads to a decrease in efficiency. torque converter by an average of 5...7%. On the other hand, to ensure the presence of a strong oil film on the friction surfaces, as well as to reduce leakage through the sealing devices, the oil must be relatively viscous.

**To obtain the largest k.k.d. hydraulic transmissions, it is recommended to use oil with a viscosity of no higher than 4...5 mm<sup>2</sup>/s at 100°C.** The use of oil with the minimum possible viscosity is also advisable because it ensures lower temperatures in hydraulic transmission due to increased circulation and increased thermal conductivity of such oil.

Another important performance indicator of HMT oil is **its anti-wear properties**. The wide variety of materials of friction pairs in HMT (steel-steel, steel-ceramic, etc.) complicates the selection of oils and additives for them.

The problem of selecting additives is due to the fact that some additives, reducing the wear of ferrous metals, cause the wear of non-ferrous metals, others vice versa. In addition, the selection of oil additives for HMP is complicated by the requirement of certain frictional properties of the oil. For the normal operation of the clutch friction discs, the oil must provide an increased coefficient of friction (from 0.1...0.2 to 0.16...0.18). With a friction coefficient of less than 0.1, the operation of the clutch discs is accompanied by their slipping, and with a friction coefficient of more than 0.18 - jerks. In both cases, this leads to premature failure of the friction discs.

The high operating temperature of the oil in the HMT, direct contact with a large amount of air in the presence of catalytically active non-ferrous metals cause rapid oxidation of the oil in the volume, thin layer and fog-like state. **Oxidation of oil**, in addition to its general pollution and increase in the content of acidic products, leads to a violation of the normal operation of individual hydraulic transmission units (friction disks). The design features of the unit, as well as the operating conditions of the vehicle, have a great influence on the oxidation of the oil in the HMT. So, for example, driving within the city limits with frequent stops and reduced driving speeds causes faster oil oxidation than driving on intercity roads.

In order to reduce the intensity of oil oxidation and to reduce the deposition of varnish and sludge on hydraulic transmission parts, **antioxidative and detergent additives** are added to oils.

Since HMT parts are made of various metals and their alloys, it is necessary that the corrosive aggressiveness of the oil to various materials is minimal. Parts made on the basis of non-ferrous metals are most susceptible to corrosion. To prevent corrosion of HMT parts, **anti-corrosion additives** are added to the oil. In addition to the minimal corrosiveness of the oil to metals, it should not have a harmful effect on rubber sealing devices, that is, should not cause excessive swelling or shrinkage of rubber parts that lead to oil leakage. Swelling of rubber from 1 to 6% is allowed.

Since HMT oil is a working body that transmits power, it is important that it maintains its uniformity during operation, that is, that it foams little. For this, **antifoam additives** are added, which can be of two types: soluble and insoluble in oil. Oil of brand A is produced for HMT.

It should also be taken into account that oil, in addition to transmitting power, ensuring reliable lubrication of all rubbing parts, and reliable operation of frictions, must also effectively cool transmission parts and, therefore, have the highest possible heat capacity. The specific heat capacity of oil for HMP in the operating temperature range is 2.08...2.12 kJ/(kg·°C).

## 11.2 OILS FOR HYDRAULIC SYSTEMS

**Working conditions.** Hydraulic oils, which will be the working fluid in hydraulic systems of automotive equipment, transmit power and actuate various units and mechanisms, as well as protect parts that rub against wear, remove excess heat, and remove wear and contamination products.

Hydraulic oils are characterized by the following operating conditions:

- ✓ large temperature drops from -30...-40 to +50...+80 °C;
- ✓ pressure in the system is 10...15 MPa;
- ✓ sliding speed up to 20 m/s;
- ✓ contact with ferrous and non-ferrous metals, seals and hoses at high pressures and temperatures.

**Operational requirements.** Hydraulic oils must have:

- ✓ good low-temperature properties (their solidification temperature should be 5...10°C lower than the ambient air temperature during the initial period of operation of the hydraulic system);
- ✓ good viscosity-temperature properties (for quick activation of the hydraulic unit, the viscosity should not be high, but on the other hand, it should be at a sufficient level) to ensure smooth operation and prevent wear;
- ✓ good lubricating properties and properties that prevent corrosion of metals and alloys, as well as the destruction of seals;
- ✓ good anti-foam properties (the ability of the liquid to release air without foaming);
- ✓ good stability during operation and storage, absence of water and mechanical impurities.

**Classification of hydraulic oils.** According to kinematic viscosity, hydraulic oils are divided into 10 classes (Table 11.1), and depending on operational properties - into 3 groups (Table 11.2).

Table 11.1 – Viscosity classes of hydraulic oils

Class viscosity	Kinematic viscosity, mm <sup>2</sup> /s, at a temperature of 40°C	Class viscosity	Kinematic viscosity, mm <sup>2</sup> /s, at a temperature of 40°C
7	4,14-5,06	32	28,80-35,20
8	6,12-7,48	46	41,40-50,60
10	9,00-11,00	68	61,20-74,80
15	13,50-16,50	100	90,00-110,00
22	19,80-24,20	150	135,00-165,00

According to the viscosity properties, hydraulic oils are conditionally divided into:

- low-viscosity – viscosity classes from 5 to 15;
- medium viscosity – viscosity classes 22 and 32;
- viscous classes – viscosity classes from 46 to 150.

Table 11.2 – Groups of hydraulic oils according to operational properties

Group oils	Oil composition	Recommended area application
A	Mineral oils without additives	Hydraulic systems with gear piston pumps operating at a pressure of up to 15 MPa and an oil temperature of up to 80°C
B	Mineral oils with antioxidant and anti-corrosion additives	Hydraulic systems with pumps of all types, operating at a pressure of up to 25 MPa and an oil temperature of more than 80°C
C	The same with anti-wear additives	The same at 90°C

*Note.* It is allowed to introduce thickening (viscosity) and antifoam additives into hydraulic oils.

The designation of hydraulic oils consists of three groups of signs: the letters MH (mineral hydraulic); numbers characterizing the class of kinematic viscosity; letters indicating the oil belongs to the group of operational properties.

For hydromechanical gearboxes, oils of grades A and R (TU 38.1011282-89) and MHT oil (TU 38.1011103-87) are used.

A-grade oil is used all-season in torque converters and hydromechanical transmissions of cars and buses. It is made on the basis of deep-cleaned oil with the introduction of anti-wear, antioxidant, depressant and anti-foam additives.

Oil of the P brand is used in hydraulic power steering of cars. Its basis is the spindle of AU oil, into which the same set of additives as in the oil of brand A is introduced.

MHT brand oil (TU 38.1011103–87) is a highly purified base, into which a complex of highly effective functional additives is introduced, providing a high viscosity index and good low-temperature properties. It is used in hydromechanical gearboxes of automotive and tracked vehicles.

### 11.3 OILS FOR TECHNOLOGICAL PURPOSES

**Industrial oils.** The oil refining industry produces a large range of modern industrial oils with high operational properties.

Industrial oils include a large group of oils intended for lubrication of friction surfaces of metalworking machines, electric motors, fans, pumps and other industrial equipment at temperatures up to 50°C. In addition, industrial oils are used as a working fluid in the power steering of a car, hydraulic systems of agricultural machines, machine tools and other equipment. The main indicator that characterizes the operational properties of industrial oils is the viscosity normalized at 40°C.

Basic operating requirements for industrial oils:

- ✓ absence of corrosive-active substances, abrasive impurities and water;
- ✓ viscosity-temperature stability and low solidification temperature.

Depending on the purpose, industrial oils are divided into four groups (GOST 17479.4–87):

- L – lightly loaded assembly units (spindles, bearings and related connections);
- H – hydraulic systems;
- S – sliding guides;

HL – heavily loaded assembly units (gears).

The designations according to the specified standard correspond to the ISO 6743/0–81 classification, groups of oils which are respectively designated by the letters F, H, G and C.

According to operational properties, industrial oils are divided into subgroups: A, B, C, D, E. For example, oils of subgroup A are oils without additives, intended for machines and mechanisms of industrial equipment, the operating conditions of which do not impose special requirements on the anti-corrosion and antioxidant properties of oils .

Depending on the viscosity, industrial oils are divided into 18 classes.

An example of the designation of an industrial oil: I-LH-A-15 (I-12A), where I is industrial, LH is for lightly loaded assembly units and hydraulic systems, A is without additives, 15 is a viscosity class, in brackets is a generally accepted designation .

The areas of application of some industrial oils are as follows:

I-LH-A-15 (I-12A) - as a working fluid in hydraulic systems of agricultural machines, hydraulic power steering of cars, in bearings of low-power electric motors, hydraulic systems of machine tools, spindles of metal-cutting machines operating with a rotation frequency of up to  $10,000 \text{ min}^{-1}$ ;

I-G-A-32 (I-20A) – hydraulic systems of construction, road and other machines, bearings of fans, pumps, spindles of drilling machines (up to  $1500 \text{ min}^{-1}$ );

I-G-A-46 (I-30A) – hydraulic systems of heavy machines, pump and fan bearings, lathes, milling machines (up to  $1000 \text{ min}^{-1}$ );

I-G-A-68 (I-40A) – hydraulic systems of heavy equipment and large machines, heavily loaded low-speed mechanisms.

**Compressor oils.** Depending on the requirements and areas of application, compressor oils are divided into three classes:

- for piston and rotary compressors;
- for turbocharged machines;
- for compressors of refrigerating machines.

For piston and rotary compressors. In these compressors, the oil is in direct contact with the compressed gas, which has a high temperature. Operational requirements for compressor oil are largely determined by the composition and properties of the gas.

According to existing standards, the air temperature after each degree of compression of air compressors should be no more than  $170^\circ\text{C}$  for general industrial compressors and no higher than  $180^\circ\text{C}$  for compressors of technological purpose. Therefore, **the main operational requirements** for compressor oils are their high thermo-oxidative stability and the ability to prevent coke formation in the compressor discharge line. The formation of these solid breakdown products and oil condensation cause compressor fires.

**Oil viscosity** is the main characteristic of compressor oils. Viscosity depends on the wear of the surfaces of the rubbing parts, the loss of frictional energy, the sealing of the piston rings, the duration of the compressor start-up, and the temperature of the friction surfaces. The formation of coke deposits depends on both the thermo-oxidative stability and the viscosity of the oil. Low-viscosity oil moves faster through the discharge path of the compressor, thanks to which less deposits are formed in the injection system. According to the rules of the International Association for Standardization (ISO), coke deposits should be removed in a timely manner. The thickness of the layer of coke deposits between cleanings of the injection system should be no more than 3 mm at a pressure of less than 1 MPa, 2 mm at 2...3 MPa and 1 mm at 3...5 MPa.

Compressor oils are divided into four groups:

- 1 – for compressors operating at moderate gas compression modes and a discharge temperature below 160°C;
- 2 – the same, at a discharge temperature below 180°C;
- 3 – for compressors operating in difficult conditions at a discharge temperature below 200°C;
- 4 – for high-pressure compressors operating in particularly difficult conditions at a discharge temperature above 200 °C.

Example of compressor oil brand designation: K-19 where K is compressor oil, 19 is kinematic viscosity at 100°C. Belongs to the first group. The oil group is indicated by a number after the letter K, except for the first group.

K-19 oil without additives is obtained from low-sulfur oils by selective purification. Used for lubrication of medium and high pressure reciprocating compressors where low-sulfur oils are required.

KS-19 oil without additives is produced from sulfurous paraffinic oils by the method of selective purification. Used for medium and high pressure piston compressors.

KS-19p oil contains the antioxidant additive "Ionol". It is obtained from sulfurous paraffinic oils by the method of selective purification. Used for lubrication of medium and high pressure piston compressors.

KZ-10 oil contains additives that reduce the formation of coke deposits in the discharge line of the compressor, as well as increase the anti-oxidation, anti-corrosion, lubricating and anti-foaming properties of the oil. Designed for lubrication of reciprocating and rotary compressors with a discharge temperature of up to 200°C.

KZ-10N oil is obtained using the same technology as KZ-10 oil, with the addition of a depressant additive to lower the solidification temperature of the oil. It has good starting properties at low ambient air temperatures. Designed for lubrication of reciprocating and rotary compressors with a discharge temperature of up to 200°C.

*For compressors of cooling machines.* Various refrigerating units are widely used in industry and agriculture, for which special oils are produced for compressors. The main features of the operating conditions of these oils: constant contact with a refrigerant (freon, ammonia, carbon dioxide); continuous change in pressure and temperature of the medium. Oils for refrigeration units must have the following properties:

- ✓ do not react with the refrigerant;
- ✓ do not cause corrosion of non-ferrous metals;
- ✓ have a gentle viscosity-temperature curve;
- ✓ have a low solidification temperature.

Highly stable oils are used in hermetic, non-disassemble compressor units of refrigerators, which work without replacement throughout the entire period of operation. Low-viscosity, deeply refined petroleum oils with an antioxidant additive and depressants, as well as oils on a synthetic basis, are most often used.

Oils for compressors of refrigerating units are divided into two groups: XA - for compressors operating on ammonia or carbon dioxide; HF - for compressors that work on freons.

***Electrical insulating oils.*** Electrically insulating oils, being liquid dielectrics, serve to insulate current-carrying parts of transformers, capacitors, cables, etc. They also serve as a heat-dissipating medium and contribute to the rapid extinguishing of electric arcs in

switches. Electrical insulating oils are divided into transformer, capacitor and cable oils. The most common transformer oils, which are used in transformer cores, rheostats, oil switches.

Transformer oil is obtained from low-sulfur and high-sulfur paraffin oils by the method of phenol purification followed by low-temperature deparaffinization. Thorough cleaning of the oil is necessary to obtain high dielectric properties (high breakdown voltage) and stability. The industry produces transformer oils of several varieties, which differ in the raw materials used, the method of production, and the field of application.

TKp oil is produced from low-sulfur oils by the acid-alkaline purification method. It contains the additive "Ionol". The kinematic viscosity of the oil at 50°C is slightly more than 9 cSt, the solidification temperature is not higher than -45°C. It is recommended to use it for equipment with a voltage of up to 500 kV.

Oil of selective purification is obtained from sulfurous paraffinic oils by the method of phenolic purification. The viscosity of the oil at 50°C is slightly more than 9 cSt, the solidification temperature is not higher than -45°C. It is used for equipment with a voltage of up to 220 kV.

T-1500U oil is produced from sulphurous paraffinic oils with the addition of the "Ionol" additive. Selective purification and hydrogenation processes are used in production. The viscosity of the oil at 50 °C is no more than 8 sSt, the solidification temperature is not higher than -45 °C. It is intended for electrical equipment with a voltage of up to 1500 kV.

GC oil is obtained by hydrocracking from sulfurous paraffinic oils, adding the "Ionol" additive. The oil has high dielectric properties and oxidation stability. It is used in high-end electrical equipment.

#### **11.4 CONTROL QUESTIONS**

1. What are the requirements for hydraulic oils?
2. How are hydraulic oils classified?
3. Where are industrial oils used?
4. What are the requirements for the operational properties of industrial oils?
5. How are industrial oils labeled? Specify the main brands of olives used in agricultural production.
6. Tell us about compressor oils and their properties.
7. Name the brands of compressor oils.
8. What are insulating oils used for?

## LECTURE 12. PLASTIC LUBRICANTS

Lecture plan:

- 12.1 General information.
- 12.2 Operational properties.
- 12.3 Classification and labeling of lubricants.
- 12.4 Assortment of plastic lubricants.
- 12.5 Control questions.

### 12.1 GENERAL INFORMATION

*Plastic lubricants* are ointment-like products that are widely used to lubricate friction nodes of various mechanisms and machines. These lubricants are essentially different from liquid mineral oils. According to their mechanical properties, plastic lubricants occupy an intermediate position *between solids and liquids*. Under the influence of small loads, they manifest themselves as solid bodies, and under high shear stresses – *as liquids*, that is, they have fluidity.

The study of plastic lubricants showed that they are colloidal systems where thickener crystals form a structural framework, 80...90% of the internal volume of which is liquid oil. A characteristic feature of plastic lubricants is the reversibility of the process of destruction of the structural frame: under the action of large loads, the frame collapses, and the lubricant works as a liquid, and when the load is removed, the frame is instantly restored and the lubricant again acquires the properties of a solid body.

*The main advantages* of lubricants over oils: the ability to stay in unsealed friction nodes, i.e. lack of fluidity at low and medium loads; better lubricating and protective properties, high efficiency. The wide spread of plastic lubricants is explained by the ability to stay in open and loosely sealed friction nodes. They are used where it is impossible to use liquid oils. The number of mechanisms and friction nodes lubricated with plastic lubricants is an order of magnitude greater than those lubricated with oil. Using lubricants instead of oils allows you to reduce the weight of the friction unit by approximately 25%. *Disadvantages of plastic lubricants* are poor cooling capacity of rubbing surfaces, lack of washout of wear products from the friction zone, difficulty of feeding to the friction unit.

*Plastic lubricant consists of two components:* an oil base (mineral, synthetic, vegetable or other oil) and a solid thickener (soap or non-soap). Lubricants usually contain a structure stabilizer and additives, often various fillers (graphite, molybdenum disulfide, powdered metals or their oxides, etc.). The thickener forms a solid structural frame, inside which the oil is contained. Such lubricants are called structured. Lubricants, which contain soft metals or their oxides, are called shocking. The thickener content in lubricants is 10...20%. The most common thickeners are metal soaps of high molecular weight fatty acids or natural fats. Using these thickeners, soapy lubricants are obtained.

There are also hydrocarbon, bentonite, silica gel and other lubricants in which solid hydrocarbons and inorganic substances serve as thickeners. These are so-called non-soap lubricants. Widespread solid lubricants, which are used at high temperatures and pressures. These include antifriction lubricants consisting of molybdenum disulfide, a binder and a volatile solvent. This lubricant is applied to the surface of the part and heated. The solvent evaporates, and a strong film remains on the surface of the part, which protects it from

wear during operation. Solid greases work at a normal temperature of 250...350°C.

## 12.2 OPERATIONAL PROPERTIES

*The main operational properties of plastic lubricants* are shear strength, viscosity, mechanical stability, thermal stability and thermosetting, colloidal and chemical stability, water resistance and the ability to prevent fretting. Along with rheological characteristics (strength and viscosity), *tribological characteristics - load and welding load* - are important for evaluating the quality of the lubricant.

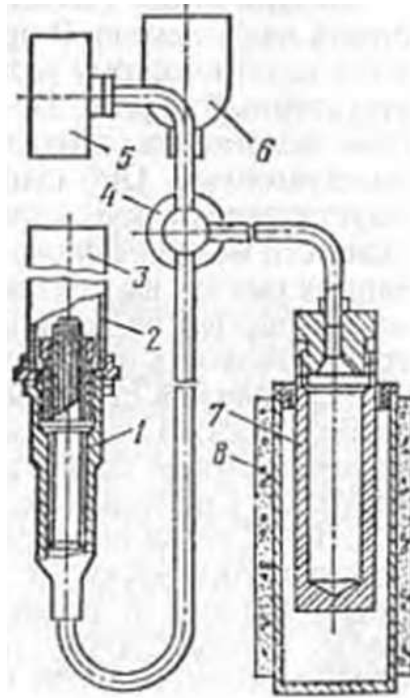
*The shear strength limit* is characterized by the minimum shear stress, at which the structural frame in the plastic lubricant is destroyed and it acquires fluidity. *The limit of the shear strength of a plastic lubricant is the critical value of the force applied to the unit area of the shear of the lubricant layers.*

The value of the shear strength limit is determined by the quality of the thickener and its concentration in the plastic lubricant. The strength limit depends on the temperature: when the temperature increases, it decreases. However, in some lubricants (for example, complex calcium, silica gel lubricants), the opposite phenomenon is observed - an increase in the strength limit with an increase in temperature. The temperature at which the strength limit becomes zero is the true temperature of the transition of the lubricant from a plastic state to a liquid state, limiting the use of plastic lubricant. The higher the shear strength of the plastic lubricant, the better it stays on the surface and the less it flows. Table 12.1 shows the value of the shear strength limit of some plastic lubricants.

Table 12.1 – Shear strength limits of plastic lubricants

Lubricants	Value of shear strength limit, Pa, at temperature	
	20°C	50°C
Solidol S	300...700	200...350
Press-solidol S	70...200	60...180
Graphite lubricant	300...700	200...300
Litol-24	500...1000	400...600
Fiol-1	≥250	200...250
TSIATIM-221	250...450	120...300
TSIATIM-201	350...500	250...350
Lubricant №158	150...500	150...300

The shear strength limit of the plastic lubricant is determined on the K-2 plastometer (Fig. 12.1), which consists of a base with a stand on which the electric furnace with oil capacity 7 moves vertically, a pressure gauge 5, a funnel 6 (for adding oil to the device) and a tap 4 (to combine the funnel with the internal cavity of the device).



1 - body; 2 - mandrel; 3 - protective glass; 4 - faucet; 5 - manometer;  
6 - funnel; 7 - oil container; 8 - electric stove.

Figure 12.1 – Plastometer K-2

Body 1 of the plastometer is connected to the internal cavity of the device by a tube. All internal cavities of the K-2 device, including the manometer, are filled with low-viscosity oil in order to completely displace air.

The strength limit (Pa) of the tested plastic lubricant is calculated according to the formula:

$$\tau = \frac{100000 \cdot pr}{2l},$$

where  $p$  – the maximum pressure determined by manometer 5 (Fig. 12.1);  $r$  and  $l$  – radius and length of the capillary. Usually  $l = 5\text{sm}$  or  $l = 10\text{sm}$ .

Both halves of the capillary chute are filled with mixed lubricant, and it is inserted into the mandrel 2. The plastometer is filled with oil, for which the tap 4 of the funnel 6 is opened and kept open until the oil level in the housing reaches the upper edge of the mandrel 2 shoulder. The electric furnace is turned on, which heats tank with oil, the increase in pressure is controlled by the manometer. After the pressure in the system, having reached a certain maximum, begins to decrease, the electric furnace is turned off, the faucet 4 of the watering can 6 is opened and the mandrel 2 with the capillary is slowly removed from the housing 1, after which the faucet is closed.

At the end of the experiment, lubricant is squeezed out of the capillary.

**Lubricant viscosity** is a variable that depends on temperature and rate of deformation. The viscosity of the lubricant is lower, the higher the temperature and the

rate of deformation. After the destruction of the structural framework, the lubricant begins to flow like a liquid. The greater the rate of deformation at a constant temperature, the faster the viscosity decreases and the fluidity of the lubricant increases. Since the viscosity of the lubricant depends on the rate of destruction of its structural frame, the concept of "effective viscosity" was introduced. It refers to the viscosity of a Newtonian fluid, which, under a given flow regime, has the same shear resistance as the lubricant.

The viscosity of the lubricant also depends on the type and concentration of the thickener, and the viscosity depends on the pumping of lubricants, energy consumption for the relative movement of lubricated parts, especially during the start-up period. Of the two lubricants, the one with the lower viscosity at the same values of the strength limit is considered to be of higher quality.

**The dynamic viscosity** of the plastic lubricant at the minimum operating temperature and deformation rate of  $10^{-1}$ s should not exceed 1500...2000 Pa·s.

**Mechanical stability** is the ability of the lubricant to resist destruction. In the process of operation, lubricants are constantly exposed to mechanical influence, as a result of which their structural framework is destroyed. During rest, the structural frame of the lubricant is involuntarily restored. This property of the lubricant is called **thixotropic**. It significantly depends on the type and concentration of the thickener, the chemical composition of the oil, the temperature of the lubricant, and the intensity of the mechanical impact. During thixotropic transformations of lubricants, their quality indicators (primarily strength) should not change. In the idle state of the friction unit, the viscosity and ultimate strength do not change or increase.

**Thermal stability and heat strengthening.** Thermal stability means the ability of lubricants to maintain their operational properties without change at elevated temperatures. The properties of most lubricants when heated to 50...100°C below the melting point and during subsequent cooling practically do not change. However, in some lubricants, after heating and subsequent cooling, the density, strength limit and viscosity increase, up to the loss of plasticity. Thermosetting has a negative effect on the operational properties of lubricants, since thermally hardened lubricants stop reaching the working surfaces due to high values of strength and viscosity limits.

**Thermosetting** of plastic grease is evaluated by measuring the strength limit before and after exposure to elevated temperature. When storing and using lubricants, liquid oil may evaporate from them. The volatility of the dispersed medium (oil) determines the service life of the lubricant. The permissible rate of evaporation of oil from a unit surface of the lubricant is about  $10^{-7}$  g/(cm<sup>2</sup>·s).

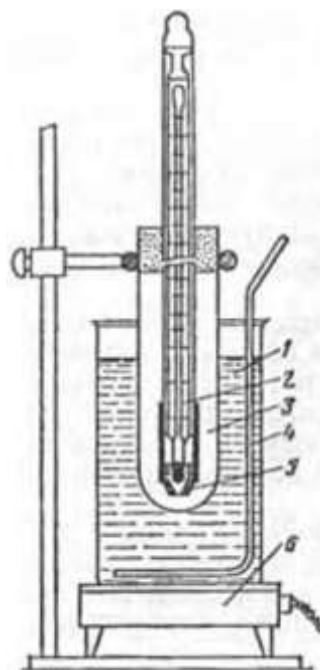
**The drop point** is the temperature at which the lubricant changes from a plastic (semi-solid) state to a liquid state. The melting of plastic lubricants is accompanied by a significant change in their properties. When determining the droplet temperature, the plastic lubricant, heated in a special device, softens to such a state that a liquid droplet is formed and falls.

Based on the temperature of the drop of lubricant (Table 12.2), it is possible to roughly estimate its performance at elevated temperatures. For reliable lubrication of friction units, it is necessary that their working temperature be 10...20°C lower than the temperature of the drop of plastic lubricant.

Table 12.2 – Dropping temperature of plastic lubricants

Lubricant	Dropping temperature, °C
Solidol S	85...105
Press-solidol S	85...95
Graphite lubricant	77...85
Litol-24	≥ 185
Fiol-1	≥ 185
TSIATIM-221	≥ 200
TSIATIM-201	≥ 175
Lubricant №158	≥ 132

The device for determining the drop temperature of plastic lubricants is shown in Figure 12.2. At the same time, a standard thermometer of the Ubbelode type is used. A metal sleeve is mounted in the lower part of thermometer 2, which is screwed into a metal tube with a hole. A capsule (cup) of 5 standard sizes is inserted into the hole. The thermometer is fixed in test tube 3 with the help of a stopper. The test tube is placed on a tripod and inserted into a beaker-bath 1, which is filled with water or glycerin.



1 - a glass with water or glycerin; 2 - a special thermometer with a sleeve;  
3 - test tube; 4 - stirrer; 5 - capsule for the tested lubricant; 6 - electric stove.

Figure 12.2 – Device for determining the drop temperature

The tested plastic lubricant is tightly applied with a spatula into the capsule, making sure that there are no air bubbles on the surface. Then the capsule is inserted into the sleeve of the thermometer so that its upper edge rests against the shoulder of the sleeve. At the same time, the lower end of the thermometer squeezes out excess lubricant through the hole. A circle of white paper is placed at the bottom of a dry, clean test tube and the thermometer is placed in the test tube so that the lower edge of the capsule is at a distance

of 25 mm from the circle. Then the tube with the thermometer is placed in the bath. Glycerin is used for lubricants with a drop temperature above 80°C. Water or glycerin is heated in such a way that after reaching a temperature 20°C below the expected drop temperature, the heating rate is 1°C per minute.

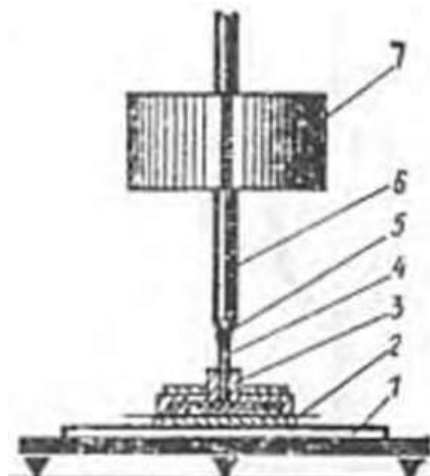
The temperature at which the first drop falls or the bottom of the test tube touches the column of lubricant protruding from the opening of the capsule is taken as the dropping temperature of the tested plastic lubricant.

**Colloidal stability** characterizes the possibility of separating the dispersion medium (oil) from the lubricant during storage and operation. The amount of oil released increases with increasing temperature and pressure. The release of oil from the lubricant is influenced by the addition of one-sided loads to it, for example, centrifugal forces and pressures. As the temperature increases, the colloidal stability deteriorates due to a decrease in the viscosity of the dispersion medium.

Plastic lubricants must release a small amount of oil when tested under certain standard conditions. Excessively stable lubricants do not lubricate friction nodes well. It is especially important to extract a certain amount of oil from the lubricant to prevent intensive wear of parts when the car moves.

The appearance of a layer of oil lying on the surface of the lubricant during storage (the phenomenon of syneresis) indicates the "aging" of the lubricant, that is, the deterioration of its operational properties. Such lubricants should be used first. Colloidal stability increases with an increase in the amount of thickener in the lubricant and decreases with a decrease in the viscosity of the mineral oil. Lubricants with low colloidal stability (for example, TSIATIM-201 lubricant) are packaged in small containers.

Colloidal stability is determined in the KSA device (Fig. 12.3) at specified loads, time and temperature. The KSA device consists of a tripod and a plate 1. A bracket is fixed on the tripod stand, which houses a rod 6 for fastening the load 7. A metal ball 5 serves to transmit pressure to the piston shank. Cup 3 for the tested lubricant, into which piston 4 is inserted, is installed on plate 1. The mass of the rod, ball, piston and load is 1 kg.



1 - plate; 2 - filter paper; 3 - cup;  
4 - piston; 5 - ball; 6 - rod; 7 - cargo.

Figure 12.3 – The working part of the KSA device for determination colloidal stability

The cup with the piston is weighed on an analytical balance, then the tested lubricant is smeared into it with a spatula, weighed and the mass of the lubricant taken for testing is calculated. One circle of filter paper is moistened with oil and weighed. A glass with a stack of filter paper (7...9 circles) is placed on the tripod table. An oil-soaked circle of filter paper is placed on top of the grease in the cup so that there are no voids between the paper and the grease, and the cup is placed on a rack of filter paper placed on the glass.

By pressing the start button, the rod is released and lowered until it collides with the ball. Then a load is put on the rod, the start button is pressed again and the test start time is noted. After 30 minutes, weigh the cup with the lubricant and a circle of filter paper.

The amount of oil (%) released after pressing the plastic lubricant will characterize its colloidal stability. The greater the amount of oil pressed out of the plastic lubricant, the lower its colloidal stability (Table 12.3).

Table 12.3 – Penetration and colloidal stability of plastic lubricants

Lubricant	Penetration number at 25°C	Colloidal stability, %
Solidol S	260...310	5
Press-solidol S	310...340	10
Graphite lubricant	250...280	5
Litol-24	220...250	12
TSIATIM-221	280...320	7
TSIATIM-201	265...310	26
Lubricant №158	310...340	23

**Penetration** characterizes the consistency or degree of softness of plastic lubricants. Penetration is determined on a laboratory LP penetrometer by the depth of immersion in the tested lubricant of a standard body (cone or needle) in shape and weight for 5 seconds at a given load and temperature. The number of penetration is expressed in whole numbers, equal to the depth of immersion of the cone or needle in the lubricant in millimeters, multiplied by 10.

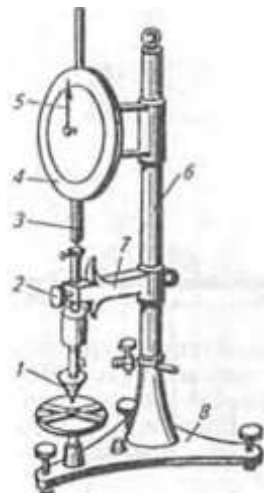
A change in the penetration of plastic lubricants during storage in operating conditions indicates a change in its structure. Such lubrication must be used sooner.

Penetration numbers at 25°C for some plastic lubricants used in motor transport are given in table 12.3.

The laboratory penetrometer LP (Fig. 12.4) consists of a tripod 6 and a plate 8, where a table is installed, the position of which can be adjusted in height. A round level gauge is built into the slab. A bracket 7 with a plunger, an indicator 4 and a mirror (not shown in the figure) are fixed on the tripod. The plunger moves freely along the guide sleeve of the bracket and is fixed with a clamp. The trigger button 2 serves to release the plunger. A cone 1 or a needle with a load is attached to the plunger. The indicator consists of a rack 3, which engages with a gear. The gear axis is connected to arrow 5.

The glass with the tested lubricant is placed on the table. With the help of a clamp, the bracket is moved along the rack so that the tip of the cone 1 touches the surface of the lubricant. The rack 3, with a spherical tip, is brought to the installed and fixed plunger

before measurement, after which the arrow 5 of the indicator is set to zero on the scale (360 divisions at the price of 0.1 mm). Then simultaneously turn on the stopwatch and press the start button 2. The cone freely sinks into the lubricant for 5 seconds, after which the button is released, stopping the immersion. The depth of immersion of the cone is determined by the indicator in tenths of a millimeter.



1 - cone; 2 - start button; 3 - rack; 4 - indicator;  
5 - arrow; 6 - tripod; 7 - bracket; 8 - plate.

Figure 12.4 – Penetrometer

**Chemical stability** is the resistance of lubricants against oxidation during storage and operation. Oxidation of lubricants reduces their anti-corrosion and strength properties, deteriorates colloidal stability, lubricating and protective capacity. When the temperature rises, the oxidation of the lubricant accelerates.

The chemical stability of lubricants is influenced by the type of thickener and the quality of the dispersion medium. The chemical stability of most inorganic and organic lubricants is higher than that of soap. In soap lubricants, oil and thickener undergo oxidation. Soaps of some metals (for example, lead) are strong oxidation catalysts.

Chemical stability is very important for long-term and "eternal" lubricants, which are filled into friction nodes once or twice during 10...15 years or once during the entire period of operation, as well as lubricants operating at temperatures above 100°C. The appearance of a hard crust on the surface of the lubricant during storage indicates its deep oxidation. Such lubricant is unusable.

Modern lubricants are prepared from high-quality oils and chemically resistant thickeners with the addition of antioxidant additives and metal deactivators.

**Moisture resistance** is primarily important for lubricants working in unsealed friction units or in contact with water. Lubricants should not be washed off with water or change their properties when moisture gets into them. When evaluating moisture resistance, the hygroscopicity of lubricants is taken into account. The properties of watered lubricants deteriorate.

Moisture resistance of lubricants depends mainly on the type of thickener. The main mass of lubricants is moisture resistant. Sodium lubricants have a low moisture resistance, preservative (protective) lubricants have a high one, and lithium lubricants have a high one.

*The anti-seize properties* of plastic lubricants are due to their ability to prevent seizing and seizing of rubbing surfaces under high loads. As the sliding speed increases, the wear of parts increases and the anti-seize effect of lubricants decreases. Additives are added to increase the anti-seize properties of the lubricant. At high contact stresses (up to 500 kN), additives with anti-friction additives such as molybdenum disulfide or graphite are used.

*The preservative properties* of plastic lubricants ensure their ability to protect metal surfaces from the effects of moisture and oxygen. The harmful effects of the atmosphere increase significantly in the country's industrial zones due to the presence of sulfur gas and other active compounds in the air. Plastic lubricants are significantly superior to mineral oils in terms of conservation properties. A layer of lubricant with a thickness of a hundredth of a millimeter prevents corrosion of metals in conditions of 100% humidity for many months.

*The ability to prevent fretting* is related to the ease of penetration of the plastic lubricant to the friction surfaces. *Fretting or fretting corrosion* is a special type of wear associated with cyclic, small displacements of rubbing surfaces. During the oscillating motion of the bearings, iron oxide is formed in the contact points of the ball with the raceway, which leads to the appearance of ulcers on these surfaces. Fretting increases with increasing load, frequency and amplitude of oscillations. However, when the amplitude of oscillations increases, the supply of lubricant to the friction zone improves and wear decreases. Lubricant easily penetrates into the friction zone on rough intersecting surfaces and microgrooves.

## 12.3 CLASSIFICATION AND MARKING OF LUBRICANTS

### Groups of lubricants

According to their purpose, plastic lubricants are divided into four groups: antifriction, conservation, rope, sealing (GOST 23258-78).

*Antifriction lubricants* are designed to reduce wear and sliding friction of connected parts. Lubricants of this group are divided into several subgroups: normal purpose for normal temperatures (working temperatures up to 70°C); general purpose for elevated temperatures (up to 110°C); multi-purpose (at operating temperatures from -30 to +130°C and for conditions of high humidity); heat-resistant (working temperatures of 150°C and higher); frost-resistant (working temperatures of -40°C and below); anti-seize and anti-wear (for rolling bearings with contact stresses above 2450 MPa and sliding bearings with specific loads above 147 MPa); chemically resistant (for friction units that work in aggressive environments); instrument; gearbox (transmission); auxiliary (molybdenum disulfide, graphite and other pastes); highly specialized (meets additional requirements for friction nodes); briquettes.

*Conservation lubricants* are designed to prevent corrosion of metal products and mechanisms during storage, transportation and operation.

*Rope lubricants* are used to prevent wear and corrosion of steel ropes, cables, organic cores of steel ropes.

*Sealing lubricants* are intended for sealing gaps, facilitating the assembly and disassembly of fittings, for stuffing devices, threaded, detachable and any movable connections, including vacuum systems. Sealing lubricants are divided into reinforcement, thread and vacuum.

### Marking of lubricants

Conventional designation of each lubricant consists of its name (solidol, lithol, graphite, etc.) and indices that briefly inform about the purpose of the lubricant, its characteristics and composition. The index designation consists of five alphanumeric indices, located in the following order: index of the group or subgroup according to the purpose of the lubricant; thickener; application temperature range; dispersion medium; grease consistency. Some indexes may be omitted. In the brand of lubricant, the indices "g, d, c" and others may be entered, denoting solid additives, respectively, graphite, molybdenum disulfide, lead, etc.

The type of thickener (index) is indicated by letters of the alphabet (Table 12.4).

Table 12.4 – Thickener type index

Thickener	Index	Thickener	Index
Soap:	M	Organic substances:	O
aluminum	Al	pigments	Pg
barium	Ba	polymers	Pl
calcium	Ca	ureas	Ur
lithium	Li	fluorocarbons	Fl
sodium	Na	Inorganic substances:	In
plumbum	Pb	clay (bentonite)	Bn
zinc	Zn	soot	So
comprehensive	Com	silica gel	Sg
soap mixture	M1 - M2	Carbohydrates are solid	Cs

**Complex soap** is denoted by the lowercase letter "k", followed by the index of the corresponding soap, for example kKa, kB<sub>a</sub>. A mixture of two or more thickeners is indicated by component indexes: Ka-I<sub>a</sub>, Li-B<sub>a</sub>, etc., and the index of the thickener that is part of the lubricant in larger quantities is put in the first place. Indices M, O, H, which mean a thickener (soap, organic substances, and inorganic substances, respectively), are put in those cases when the thickener is not provided for in the list.

The temperature interval of application is indicated by a fraction, the numbers of which correspond to the temperature reduced by a factor of 10. For example, 3/13 means that this lubricant can work in the temperature range from -30 to +130°C. The minimum temperature is considered to be the temperature at which the viscosity of the lubricant does not exceed 2000 Pa·s. The type of dispersion medium is denoted by the following indexes: petroleum oil - n, synthetic hydrocarbons - y, esters - e, fluorosiloxanes - f, organosilicon liquids - k, halocarbon liquids - z, perfluoroalkyl polyesters - a, other oils and liquids - p.

The presence of solid additives in the lubricant is indicated by letters: graphite - g, molybdenum disulfide - d, lead powders - c, copper powders - m, zinc powders - c. Other solid additives - i.e.

A mixture of two or more oils is denoted by an index (PC, UE, etc.), and the index of the oil, which is part of the dispersion medium in larger quantities, is put in the first place. The "n" index is used when synthetic or other oil, which is part of the dispersion medium, is not listed. In the manufacture of lubricants based on petroleum oil, the "n"

index is not indicated. It is introduced into the brand when marking a lubricant made from a mixture of petroleum and any other oil.

The consistency class of plastic lubricant is indicated by an Arabic numeral. According to the amount of lubricant penetration, 9 consistency classes are assigned (Table 12.5).

Table 12.5 – Penetration of lubricants depending on consistency class

Penetration number at 25°C	Consistency class
400...430	00
335...385	0
310...340	1
265...295	2
220...250	3
175...205	4
130...160	5
85...115	6
Ниже 70	7

Examples of designation of three lubricants and their decoding:

Lubricant MLi4/13-3,

where M is a multipurpose lubricant; Li - thickener - lithium soap; 4/13 – temperature range of application from –40 to +130°C; Consistency class 3 (penetration at 25°C is 220...250);

Lubricant SKa2/7-2,

where C is a general-purpose antifriction lubricant used at temperatures up to 70°C (solidol); Ka - thickener - calcium soap; 2/7 – the recommended temperature range of use is from –20 to +70°C (lubricant viscosity at –20°C is close to 2000 Pa·C); there is no dispersion medium index, so the lubricant is made on petroleum oil; 2 – lubricant consistency class (penetration at 25°C is 265...295);

Lubricant KT6/5k-g4,

where A is rope lubricant; T – thickener – solid hydrocarbons; 6/5 – operating temperature range from –60 to +50 °C; ko – grease made on the basis of organosilicon liquid; d – graphite used as an additive; 4 – lubricant consistency class (penetration at 25°C is 175...205).

## 12.4 ASSORTMENT OF PLASTIC LUBRICANTS

*The main component of lubricants is a thickener*, which determines their main operational properties. In our country, the following types of lubricants are produced (by thickener): soap (lithium, complex lithium, sodium and sodium-calcium, anhydrous calcium, complex calcium, aluminum, etc.), non-soap (inorganic and organic), hydrocarbon.

The structure of the release of plastic lubricants through the thickener determines the level of their quality in general.

### General purpose lubricants for normal temperatures

**Solidol synthetic** is prepared by thickening industrial oil with calcium soaps of synthetic fatty acids obtained by oxidation of paraffin. In addition to the mandatory two components – the dispersion medium (oil) and the dispersed phase (thickener), the composition of solidols includes a third component - a structure stabilizer, which is served by water. Therefore, the maximum temperature of use of solidols is 65 °C. At higher temperatures, they are irreversibly destroyed.

**Synthetic solidols** are produced in two brands: solidol C and press-solidol C. Solidol C is fed into friction units of machines operating at temperatures up to -10°C, and press-solidol C - at normal temperatures up to -30°C. The advantages of solidols are high moisture resistance and good protective properties. Solidols are used in assembly units of cars, agricultural machines, and machine tools. Disadvantages of solidols include low operating temperatures and poor mechanical stability.

**Fatty solidol** is obtained by thickening with calcium soap fatty acids that are part of natural fats. This solidol is produced in two brands: solidol Z and press-solidol Z. Several better viscosity-temperature characteristics of fatty solidols lead to their wider use compared to synthetic ones. However, in most cases, fatty and synthetic solidols are interchangeable. When mixing fatty and synthetic solidols in any ratio, their operational characteristics do not deteriorate. Substitute – Litol-24.

**Graphite lubricant** is a black ointment. This is a calcium hydrogenated grease with the addition of 10% soft flaky graphite. Despite its poor low-temperature properties, the lubricant is used all-season in heavily loaded low-speed mechanisms, where the increase in resistance caused by the lubricant is of no practical importance (in car springs, open gears, torsion suspensions of tracked vehicles, etc.). It is unsuitable for precision joints and rolling bearings. The lubricant is operable at a temperature of -20...+70°C. Substitutes are – solidol C, solidol Z or Litol-24 with the addition of 10% graphite.

### General purpose lubricants for elevated temperatures

**Konstalin** (universal refractory lubricant UT) is produced in two brands: Konstalin-1 and Konstalin-2, which differ in droplet temperature and penetration rate. Fatty constalins are obtained by thickening the purified or leached mineral number with sodium soaps. They are used for rolling bearings operating at temperatures up to 110°C (in wheel hubs, cardan shafts, axles and hinges of control pedals, electric motors). Substitutes – Litol-24, Litol-459/5.

**1-13** – a mixture of petroleum oils of low and medium viscosity, thickened with sodium soap and fatty acids of castor oil. Contains a small amount of calcium soap. The lubricant is usable at a temperature of -20...+110°C. It is used to lubricate rolling bearings of electric motors, wheel hubs of outdated cars. Substitute – Litol-24.

**Litin-2** is a mineral oil thickened with lithium soap of 12-oxystearic acid and aerosol. The oil contains antioxidant, anti-seize, anti-wear, adhesive and anti-corrosion additives, has high tribological and adhesive properties. Workable at temperatures of -40...+120°C. Designed for lubrication of needle bearings of cardan joints and other friction components of cars. Substitute – Litol-24.

### Multipurpose lubricants

**Litol-24** is a brown or cherry-colored lubricant that is mineral oil thickened with stearic acid lithium soap. The composition of the lubricant includes viscous and

antioxidant additives. Litol-24 has high moisture resistance and is not prone to thixotropic thermal hardening. It has high colloidal, chemical and mechanical stability. Water resistant, does not dissolve in boiling water. Workable at a temperature of -40...+120°C.

Lubricant is used in friction units of cars, electric, road construction, agricultural and other machines, successfully used in needle bearings of cardan joints.

In connections that are not protected from dirt and water, it is not advisable to use Litol-24 lubricant, as well as other high-quality lubricants. Litol-24 replaces many lubricants: solidols, cardan AM, etc. If Litol-24 is used in closed assembly units (wheel hubs, water pump bearings, etc.) instead of general-purpose lubricants, the terms of lubrication work are increased by more than 2 times. Substitute – Litol-24RK.

**Litol-24RK** is a mixture of mineral oils thickened with lithium soap of hydroxystearic acid. The composition of the lubricant includes anticorrosive, viscous, antioxidant and protective additives. The grease is water-resistant, provides preservation of friction nodes for 10 years, is operable at a temperature of -40...+120°C. Used for lubrication of rolling and sliding bearings of all types of wheeled and tracked vehicles, electric machines. Substitute – Litol-24.

**LKMtrais-2** is a mixture of mineral oils thickened with complex lithium soap. Water resistant, contains multifunctional additives. It has high thermal and mechanical stability, as well as good anti-corrosion and lubricating properties. Workable at temperatures of -40...+150°C, briefly up to 170°C. It is used for lubrication of friction units of vehicles and industrial equipment. Substitute – Litol-24.

**Taurol-2** is a mixture of mineral oils thickened with lithium soap of fatty acids. Contains viscous and anti-corrosion additives. It has high thermal and mechanical stability. Workable at temperatures of -40...+150°C, short-term up to 170°C. It is used for lubrication of friction units of vehicles and industrial equipment. Substitute – Litol-24.

#### Automotive lubricants

**Fiol-2U** is petroleum oil thickened with lithium hydroxystearate. Contains an antioxidant additive and an anti-friction additive. It has high antioxidant, mechanical and colloid stability, good anti-wear and anti-scratch properties. Waterproof, operable at temperatures of -40...+120°C. It is used to lubricate the needle bearings of the cardan shaft of cars. Substitutes – SHRUS-4, lubricant №158.

**Litol-459/5** is a mineral oil thickened with lithium soaps of stearic and 12-hydroxysarinic acids. Contains an antioxidant additive. Water resistant, operable at temperatures of -40 ... +120°C, short-term up to 130°C. It is used to lubricate the breaker-distributor of the car ignition system.

**LTS-15** is a mixture of mineral oils thickened with lithium soap and hydrogenated castor oil acids. Contains antioxidant and viscosity additives and zinc oxide. It has fairly good thermal, colloidal and antioxidant stability, as well as preservative and adhesive properties. Waterproof, operable at temperatures of -40...+130°C. It is used for lubrication of hinges and axles of the accelerator drive, switching levers, splined joints, window mechanisms of cars. Substitute – Litol-24.

**SHRUS-4** – mineral oil thickened with lithium hydroxystearate. Contains antioxidant and anti-seize additives, as well as anti-friction additives. Water resistant. It has high mechanical and antioxidant stability, as well as anti-wear and anti-scratch properties. Workable at temperatures of -40...+120°C. Designed for lubrication of joints of

equal angular velocities of all-wheel drive cars and other friction nodes. Substitute – lubricant №158.

**Lubricant №158** is a mineral oil thickened with lithium-calcium soap of castor oil acids and rosin. Contains an antioxidant additive. It has good antioxidant and mechanical stability, high anti-wear properties. Water resistance is satisfactory. Workable at a temperature of -30...+110°C. It is intended for lubrication of rolling bearings of auto-tractor equipment, bearings of needle cardan joints of non-constant angular speed. Lubrication is placed in closed bearings (for example, in the clutch release bearing of trucks) and is not replenished throughout their service life. Substitute – SHRUS-4.

**Cardan lubricant AM**, obtained by thickening mineral and castor oil and rosin with calcium soap, is intended for lubrication of cardan joints of front driving axles of cars. Since this lubricant is washed out of friction nodes, the temperature range of application is from -20 to +100°C. Substitutes – Litol-24, SHRUS-4.

#### **Instrument and protective lubricants**

**TSIATIM-201** is an instrument lubricant, namely vanillin instrument oil (MVP), thickened with stearic acid lithium soap and containing an antioxidant additive. The lubricant is usable from -60 to +90°C. It is used in rolling and sliding bearings, guide joints, friction units of cars and tractors that work with a small shear force at low loads.

**PVK** is a hydrocarbon protective lubricant from yellow to brown in color, obtained by fusing petrolatum with viscous residual oil with the additional introduction of 5% ceresin and an additive. Lubricant is used for ferrous and non-ferrous metals of any shape and size. It has high water resistance and stability, insoluble in water. Metal parts are immersed in melted grease or PVK is applied to the part with a brush at temperatures not lower than 10°C. Workable at temperatures from -50 to +45°C. The shelf life of parts preserved with this lubricant is 10 years.

### **12.5 CONTROL QUESTIONS**

1. What is the composition of plastic lubricants?
2. Name the operational properties of plastic lubricants.
3. What groups are lubricants divided into according to purpose?
4. How are plastic lubricants marked?
5. Tell us about the composition and scope of application of solidols and Litol-24 lubricant.
6. What is the purpose of PVK hydrocarbon protective lubricant?

## LECTURE 13. TECHNICAL LIQUIDS

Lecture plan:

- 13.1 Cooling liquids.
- 13.2 Brake liquids.
- 13.3 Damping liquids.
- 13.4 Starting liquids.
- 13.5 Control questions.

### 13.1 COOLING LIQUIDS

During the operation of the engine, some parts, coming into contact with hot gases, become very hot. The high temperature of pistons, cylinders, heads and valves leads to increased soot and varnish formation, increased friction, burrs and wear of parts. For the normal operation of the engine, the temperature of the parts must be maintained at a certain level. This is provided by the cooling system, which, depending on the speed and power of the engine, removes 15...35% of the heat generated during fuel combustion. In gasoline and gas engines, the share of heat that is removed is always greater than in diesel engines. The temperature in the cooling system must be maintained at a certain level in accordance with the manufacturer's instructions for this brand of engine.

The good operation of the cooling system depends on the correct choice and quality of the coolant.

***Coolants must meet the following requirements:***

- efficiently remove heat (that is, have a high heat capacity and low viscosity);
- have a high boiling point and heat of vaporization;
- have a low crystallization temperature;
- do not form deposits in the cooling system;
- do not cause corrosion of metal parts;
- do not destroy the rubber parts of the cooling system;
- do not foam while working;
- to be cheap, fireproof and harmless to health.

**Use of water as a coolant**

The most common liquid used for cooling is water. It has the highest heat capacity of 4.19 kJ/(kg·°C), higher thermal conductivity, small kinematic viscosity ( $\nu_{20^\circ\text{C}} = 1 \text{ mm}^2/\text{s}$ ) and higher heat of vaporization.

**Water**, which is widely used as a coolant, along with such advantages as high heat capacity, affordability, fire safety and harmlessness to humans, has a number of significant disadvantages. The main disadvantage is the high freezing temperature (0 °C). At the same time, ***the water increases in volume by about 10%***, as a result of which the cylinder heads, blocks and radiators may burst, since the ice when expanding presses on the walls of the system with a pressure of about 245 MPa. The threat of water freezing in the cooling system creates great difficulties during the operation of engines in winter. ***A relatively low boiling point should also be attributed to the disadvantages of water.***

The temperature of the cooling water in tractor engines is maintained at 80...90°C.

**Water has corrosive properties.** It contains dissolved gases and some salts that corrode metals. Oxygen, carbon dioxide and hydrogen sulfide are highly corrosive. Water

in the cooling system forms sludge and scale.

When using water as a coolant, *the formation of deposits* in the engine cooling system is determined mainly by the presence of salts dissolved in water, which form scale, the thermal conductivity of which is approximately 100 times less than the thermal conductivity of steel. The deposit of scale in the cooling system (Fig. 13.1) causes a violation of the thermal regime of the engine, an increase in fuel and oil consumption.

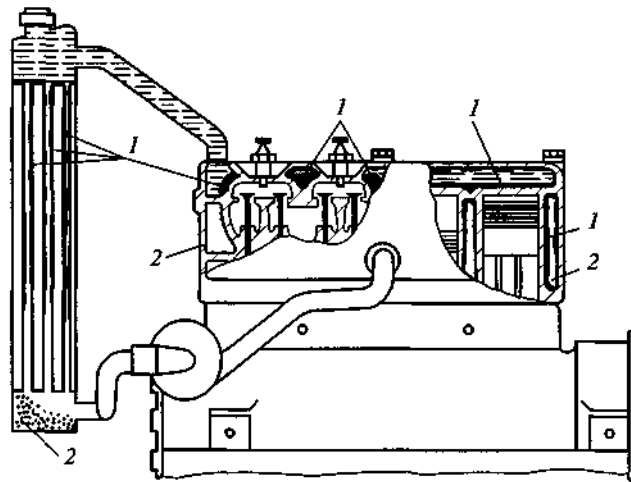


Figure 13.1 – Typical locations of deposits of scale (1) and sludge (2) in the cooling system of automobile engines

**Scale** is a dense, strong deposit formed on the hot walls of the cooling system jacket due to the precipitation of various salts from the water. **Sludge** is called muddy deposits of mineral or organic origin, which gradually coagulate and settle in stagnant zones of the cooling system. Sludge and scale reduce the cross-section of the channels and have a very low thermal conductivity, which dramatically reduces the removal of heat from the cooling parts. With large deposits of scale and sludge in the engine jacket, heat removal from the cylinder walls can decrease by 40%. This leads to overheating of the engine, the viscosity of the oil decreases, the lubrication conditions of parts deteriorate, wear increases, and the tendency of gasoline to detonation increases. Gasoline engines increase fuel consumption.

Atmospheric water (snow, rain) is the cleanest. It does not contain dissolved salts and organic substances, but dissolved gases are always present. There are significantly more dissolved salts in river water than in marsh and pond water. The latter are dominated by organic substances.

The tendency to scale formation in the cooling system is characterized by the hardness of the water due to the content of calcium and magnesium ions in it. The unit of water hardness is moles per cubic meter ( $\text{mol}/\text{m}^3$ ). There is a distinction between removable and non-removable water hardness.

The removable hardness of water is due to the presence in the water of carbonate and bicarbonate ions of calcium and magnesium salts, which are removed during boiling. These salts can be dissolved in water only in the presence of carbon dioxide. In the process of boiling water, carbon dioxide decomposes, and salts break down and precipitate. The higher the temperature of the cylinder block walls, the faster the decomposition of salts and the

formation of scale. Water softens, and its hardness is eliminated.

Permanent hardness is caused by the presence of salts in water that do not decompose when boiled, but they precipitate and participate in the formation of scale when part of the water evaporates from the cooling system, when their concentration exceeds the saturation limit. Water is considered soft if the total salt content in it is  $3 \text{ mol/m}^3$ , moderately hard -  $3...6 \text{ mol/m}^3$ , and hard - more than  $6 \text{ mol/m}^3$ . ***Hard water is unsuitable for engine cooling systems.***

Water hardness is usually determined in laboratory conditions, but it can also be estimated in a simple way. So, in soft water, a stable soapy foam is formed, in water of medium hardness, foam is formed during prolonged soaping, and in hard water, it is not formed at all. As a rule, in the northern regions of our country, the waters are soft. The more southern the area, the higher the hardness. In the southern regions, water hardness is sometimes  $80...100 \text{ mol/m}^3$ .

In internal combustion engines, it is necessary to use only soft water that almost does not form scale. Before filling the cooling system, water must be filtered to remove mechanical impurities.

Water of medium and hard hardness should be softened in various ways. The simplest of them is boiling. Boiled water should be filtered through a dense cloth to remove sediment. With chemical methods of water softening, all salts turn into sediment, which is then removed by settling and filtration. Solutions of soda and lime, trisodium phosphate, hexametaphosphate and other reagents are used to soften water. A widely used cationic method. Cations are substances that can exchange their cations for cations of salts dissolved in water, as a result of which scale does not form. It is possible to prevent the formation of scale in the engine cooling system directly by introducing special additives into the system, for which chromepeak and sodium phosphates are used, which convert scale-forming salts into loose precipitates.

#### **Low-freezing cooling liquids**

***Low-freezing coolants*** - antifreezes (from the English "antifreeze" - non-freezing) have replaced water in the engine cooling systems of modern cars. Low-freezing liquids based on glycol, which is a mixture of ethylene glycol and water, have become the most widespread. Sometimes there are liquids based on ***propylene glycol*** - ***they cannot be mixed with ethylene glycol.***

As mentioned above, low-freezing coolants (ethylene glycol antifreezes) are widely used as coolants for automobile engines.

***Ethylene glycol*** – is a diatomic alcohol ( $\text{CH}_2\text{OH}-\text{CH}_2\text{OH}$ , or  $\text{C}_2\text{H}_4(\text{OH})_2$ ), which is a poisonous, oily, yellow, odorless liquid. It mixes well with water in any ratio and freezes at  $-11.5 \text{ }^\circ\text{C}$ . However, when mixing ethylene glycol with water, the solidification temperature of the mixture is lower than that of each component separately. When mixing ethylene glycol with water in various ratios, it is possible to obtain mixtures that freeze from  $0$  to  $-75 \text{ }^\circ\text{C}$ . As ethylene glycol is added to the water, the temperature of the mixture decreases. The minimum temperature of the mixture is reached when it contains 33% water. A further decrease in the content leads to an increase in the freezing point (Fig. 13.2).

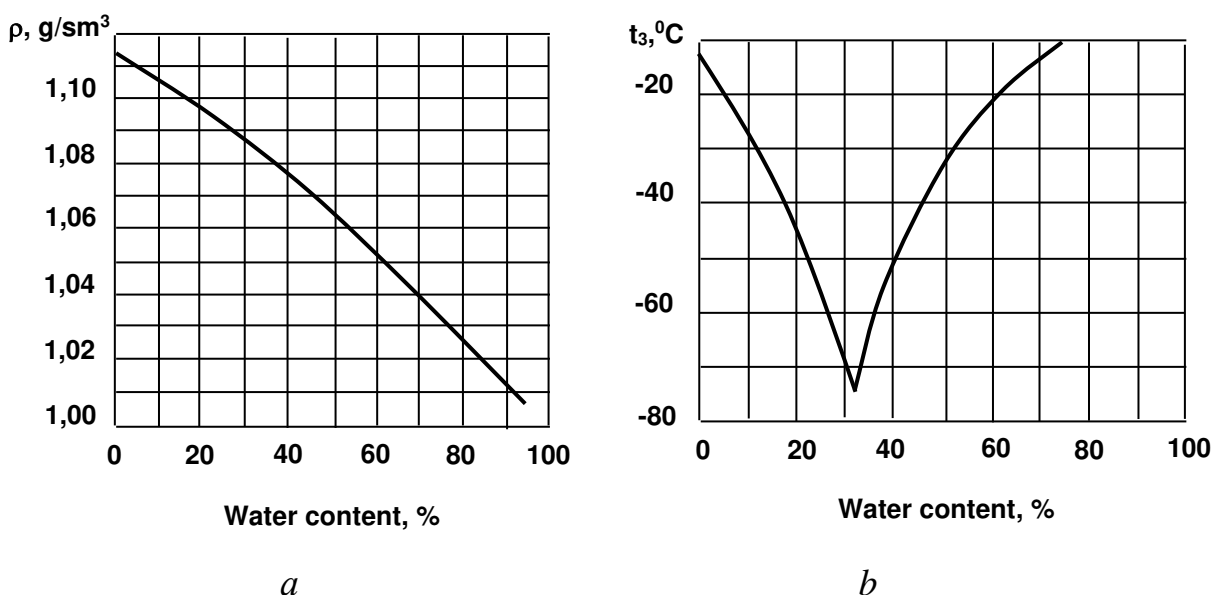


Figure 13.2 – Dependencies of the density  $\rho$  at 20°C (a) and the freezing temperature  $t$  of antifreezes on their water content (b)

Since the densities of ethylene glycol and water are different, mixing them in different ratios changes the density of antifreeze. Its freezing point can be determined by the density of the coolant.

Low-freezing cooling liquids include aqueous solutions of ethylene glycol with anti-corrosion, anti-foaming, stabilizing additives and dyes. They are made by the following brands:

**Coolant (concentrate)** – slightly more than 5% water, density 1100... 1150 kg/m<sup>3</sup>. When adding distilled water to the concentrate in a volume ratio of 1:1, the crystallization temperature of the solution is -35°C;

**Coolant-65** – density 1085... 1100 kg/m<sup>3</sup>, the beginning of crystallization is not higher than -65°C;

**Coolant-40** – density 1065... 1085 kg/m<sup>3</sup>, the beginning of crystallization is not higher than -40°C.

"TOSOL" is one of the names of antifreeze, formed from two parts: "TOS" - "Technology of Organic Synthesis" (the name of the Department of the State Research and Development Institute of the State of Ukraine, which created the antifreeze); "OL" is an ending characteristic of alcohols (ethanol, butynol, methanol).

This antifreeze was developed in 1971 at the State Research Institute of Organic Chemistry and Technology (State Research Institute of Organic Chemistry and Technology) for VAZ cars instead of the Italian "PARAFILU". The "TOSOL" trademark was not registered, so it is used by many domestic manufacturers of coolants. But the operational properties of "antifreezes" can be different, as they are determined by the additives used, and they differ among different manufacturers.

The characteristics of low-freezing coolant "Tosol" are given in table 13.1.

Table 13.1 – Main indicators of coolant "Tosol"

Indicator	«Tosol AM»	«Tosol A-40M»	«Tosol A-65M»
Color	Blue	Blue	Red
Density at 20°C, kg/m <sup>3</sup>	1120... 1140	1075... 1085	1085... 1095
The temperature of the beginning of crystallization, °C, is not higher	—	– 40	– 65
Corrosion losses of metals at tests, kg, no more:			
copper	10	10	10
solder	12	12	12
aluminum	20	20	20
cast iron	10	10	10
Storage, %:			
ethylene glycol	97	56	64
water	3	44	36

Sometimes sodium molybdenum in the amount of 7.5...8.0 g per liter is added to simple antifreezes, which prevents corrosion of zinc and chrome coatings on parts of the cooling system. At the same time, the letter "M" is added to the designation of antifreeze.

The composition of cooling low-freezing liquids is determined by a hydrometer (Fig. 13.3), which has a double scale - the content of ethylene glycol and the freezing temperature.

The cooling liquid is poured into a glass cylinder and the hydrometer is carefully lowered. After the hydrometer is installed, the values of the composition of the coolant and the solidification temperature are read on the scale at the upper limit of the meniscus. The temperature of the coolant should be 20°C.

**All cooling low-freezing fluids are used all season.** When using them in internal combustion engines, some features should be taken into account. When the engine is running, the first thing that evaporates from the cooling system is water, which must be periodically added. If there is a coolant leak from the cooling system, you need to add antifreeze.

Coolants have a high volumetric expansion coefficient, so do not add 6...8% liquid to the cooling system. When the coolant freezes inside the engine cooling system, a porridge-like loose mass is formed, the volume of which increases very little (by approximately 0.25%), as a result of which there is no danger of engine defrosting. The ingress of gasoline, oil, and other petroleum products into the coolant causes strong foaming and liquid ejection through the radiator plug from the cooling system.

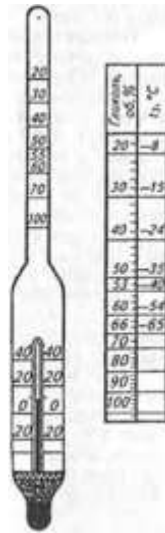


Figure 13.3 – Hydrometer and its scale

Ethylene glycol coolants have a lower heat capacity than water. Therefore, when replacing water with coolant in the engine cooling system, higher temperatures are allowed. Coolants have great mobility and permeability, cause some softening of the rubber. In this regard, it is necessary to carefully monitor the condition of the connecting hoses of the cooling system. Since ethylene glycol coolants are poisonous, precautions should be taken strictly when working with them. The liquid cannot be sucked in by mouth to create a siphon, the cooling system must be filled carefully, preventing spillage and overflow of the liquid. Before eating, hands contaminated with coolant must be washed with soap, since when it gets into the human body, severe poisoning occurs, sometimes with a fatal outcome.

#### **International standardization of coolants**

To protect their consumers, large countries set special quality standards for coolants. Coolants that have passed inspection and tests by car manufacturers and standardization bodies are given the appropriate certificates – *standards*.

The requirements for foreign-made antifreezes are usually determined by the *standards of ASTM* (American Association for Testing Materials) and *SAE* (Society of Automotive Engineers). These standards regulate the properties of concentrates and antifreezes based on their base (ethylene glycol or propylene glycol) and operating conditions. For example, ethylene glycol liquids are intended for:

- according to ASTM D 3306 and ASTM D 4656 - for cars and small trucks;
- according to ASTM D 4985 and ASTM D 5345 - for engines operating in severe conditions: long-term operation in modes close to maximum power, on off-road equipment, large trucks, stationary power plants, etc. These liquids differ in that a special additive must be added before use.

ASTM D 3306 imported antifreeze can be used for domestic cars.

Here are examples of some recognized international standards:

- ASTM D 3306; ASTM D 4340; ASTM D 4985; SAE J1034 (USA)
- BS 6580; B5 5117 (Great Britain)
- JIS K 2234 (Japan)

- AFNOR NF R 15-601 (France)
- FVV HEFT R 443 (Germany), etc.

Since the beginning of the 90s of the last century, traditional antifreezes have been replaced by antifreezes of a new generation, made on the basis of carboxylate technology. In addition to ethylene glycol and water, these antifreezes contain packets of corrosion inhibitors based on the composition of salts of mono and dicarboxylic acids. Such coolants most fully meet the requirements of motorists for coolants. They have a high boiling point, a low freezing point, reliably protect the metal parts of the car cooling system from corrosion, have good compatibility with rubber and plastic components of the system, and a long service life (up to 5 years).

### **International classification of cooling liquids**

As we have already mentioned, modern antifreezes include ethylene glycol, water and additives. The basic components, water and ethylene glycol, make up 93-97% of the liquid volume, the rest are additives. It is the additives that determine anti-corrosion and anti-cavitation properties of antifreeze, its service life and cost. ***And antifreezes of different classes and manufacturing companies differ from each other in terms of additives.***

***Antifreezes are produced either in the form of concentrates or in the form of ready-to-use liquids.*** Antifreeze concentrate contains only ethylene glycol and additives. It is assumed that the consumer will add water himself, and the optimal ratio of concentrate and water is 50:50 for our latitudes. Ready-to-use liquids already contain the required amount of demineralized water and are designed for the temperature of the beginning of crystallization depending on the climate in which the vehicle is operated.

In Ukraine and the post-Soviet space, the standard of the Volkswagen company is accepted for the classification of antifreezes. It provides for the division of coolants into classes based on the composition of additives into ***traditional, hybrid and carboxylate.***

***Traditional antifreezes (class G11)*** contain ethylene glycol and inorganic additives (silicates, phosphates, borates, amines, nitrites) and are currently considered obsolete, since inorganic inhibitors have a short (no more than 2...3 years or 45...60 thousand . km mileage) service life and cannot withstand high (over 105°C) temperatures. During operation, silicates cover the entire inner surface of the cooling system with a silicate layer, which worsens heat exchange and reduces the efficiency of engine cooling. Silicate antifreezes also do not protect against cavitation. Today, they are used in old models of cars and in cars that have served their time, for which the main advantage of coolant is its cheapness. They are classified as antifreeze for cars manufactured before 1996. Traditional antifreezes include all kinds of variations of Tosol.

Unlike traditional antifreezes, the service life of ***hybrid antifreezes (class G12)*** is longer – on average 3...5 years, or 250,000 km of mileage. Their additive packages also include salts of carboxylic acids and small additions of silicates (European technology) or phosphates (Japanese and Korean technology). In the technical literature, hybrid antifreezes are designated as: Hybrid Technology, NF (Nitrite Free), G12 (according to the VW TL 774C specification). This class of antifreeze has its subclasses G12+ and G12++, which differ in the composition of additives or the base.

**Class G12.** Antifreeze based on organic carboxylate compounds. They are classified as antifreeze for cars manufactured in 1996-2001. They are best suited for high-speed and temperature-loaded engines. The maximum service life of antifreezes of this class is about 5-6 years.

**Class G12+.** Classified as antifreeze for cars from 2001. They do not contain nitrites, phosphates, borates, silicates, amines.

**Carboxylate antifreezes (class G13)** are considered better in terms of their lubricating and anti-corrosion properties, freezing and boiling points, less aggressiveness towards such parts as oil seals, gaskets, pipes, etc., as well as a long service life. Carboxylic acid salts are the basis of carboxylate antifreeze additives. Carboxylate antifreezes are used in most of the world's car factories for the first filling of modern cars, as well as in service centers during maintenance. They meet the requirements of the VW TL 774F (G12+) specification. In the technical literature and in the names of antifreezes, the following terms are used to denote carboxylate technologies: OAT (Organic Acid Technology), LLC (Long Life Coolant), XLC (eXtended Life Coolant), SNF (Silicate Nitrite Free), SF (Silicate Free), G13 (according to VW TL 774D specification). Carboxylate antifreezes can be used for a long period of time - more than 5 years, with mileage of more than 250,000 km in cars and 650,000 km in trucks. Antifreeze uses propylene glycol instead of ethylene glycol. This is a more ecological product (non-poisonous, decomposes faster). But also more expensive. This is a group of antifreezes for forced/sports engines of cars and motorcycles operating in extreme conditions. Because of its high cost, it is not produced in the CIS countries.

## 13.2 BRAKE LIQUIDS

### Purpose and characteristics of brake fluids

**The purpose of brake fluid** is to transfer energy from the brake master cylinder to the wheel cylinders, which press the brake pads to the brake discs or drums. The pressure in the brake hydraulic drive reaches 10 MPa, and the fluid temperature in the disc brakes is 150...190°C. During operation, moist air enters the brake system through the rubber seals, as a result of which the brake fluid is moistened and its boiling point decreases. If the boiling temperature of the liquid falls below 150°C during the operation of the car, gas bubbles and vapors are released in it, forming vapor plugs. This can lead to brake failure and an accident. **The boiling point of the brake fluid** is the main indicator that determines the maximum permissible operating temperature of hydraulic brake actuators.

During the operation of the car, the boiling point of the brake fluid gradually decreases due to waterlogging. Therefore, the temperature of the moistened liquid containing 3.5% water is determined. This indicator indirectly characterizes the temperature at which the liquid will "boil" after 1.5...2 years of operation in the brake hydraulic drive.

**On all cars, the brake system has a hydraulic drive, the reliability of which depends on the quality of the brake fluid.**

**Operational requirements for brake fluids** are as follows: fairly high boiling point; high mobility, low viscosity; the freezing temperature is lower than the ambient air temperature; preservation of homogeneity, i.e. the brake fluid should not be stratified and

clots and sediment should not fall out in it; full compatibility with rubber parts and metal of the braking system; good lubricating ability.

Modern brake fluids are mixtures of ethers with polymers and additives. BSK, Neva, Tom, Rosa, Rosa-3, Rosa DOT-3, and Rosa DOT-4 liquids are produced in the CIS (Table 13.2).

Table 13.2 – Characteristics of brake fluids

Indicator	«Neva»	«Tom»	"Rosa", "Rosa-3", "Rosa DOT-4"	BSK
Appearance	Transparent homogeneous liquid from light yellow to dark yellow without sediment. Slight opalescence is allowed*			Transparent homogeneous liquid of orange-red color
Kinematic viscosity, mm <sup>2</sup> /s at temperature:				
50°C, not less	5	5	5	9
100°C, no less	2	2	2	–
- 40°C, no more	1500	1500	1450	2500
Low-temperature properties: the appearance of exposure (6 h, -50°C)	Transparent liquid without stratification and sediment			
The time of passage of an air bubble through a layer of liquid when the vessel is overturned, s, no more	35	35	8	–
Boiling temperature, °C, not lower	195	220	260	115
Boiling temperature of "moistened" liquid, °C, not less	138	155	165	110
The content of mechanical impurities, %	There are no			
pH	7,0...11,5	7,0...11,5	7,5...9,0	≥6
The interaction with metals, estimated from the change in the mass of the plates, mg/cm <sup>2</sup> , not more:				
white plate	0,1	0,1	0,1	0,2
steel 10	0,1	0,1	0,1	0,2
aluminum alloy D-16	0,1	0,1	0,1	0,1
cast iron 18	0,1	0,08	0,1	0,2

Continuation of table 13.2

brass L62	0,4	0,1	0,2	0,4
copper M1	0,4	0,2	0,2	0,4
Impact on rubber, %:				
volume change of 7-2462 rubber at 70°C	2...10	2...10	2...10	5...10
volume change of 51-1524 rubber at 120°C	2...8	2...10	2...10	—
Change in strength limit of rubber brand 51-1524, %,	20	18	25	—

\* Opalescence – is a bright blue glow.

Do not mix fluids made on different bases, as this leads to stratification of the brake fluid and deterioration of its operational properties. If the brand of hydraulic fluid poured into the brake system is unknown, a mixing test is performed. The fluid from the braking system and the fluid to be added to the system are poured into the test tube in equal quantities. Then they are shaken. If the mixture has separated, you cannot add brake fluid to the system.

**BSK brake fluid** is transparent, homogeneous, red in color, without precipitation and mechanical impurities. It is a mixture of 50% castor oil and 50% butyl alcohol. The density of the liquid at 20°C is 890...900 kg/m<sup>3</sup>, the kinematic viscosity at a normal temperature of 50°C is within 9...13cSt. Due to the presence of castor oil, the liquid has good lubricating properties, does not cause large swelling or softening of the rubber sealing parts of the brake system. However, the viscosity-temperature properties of this liquid are unsatisfactory, so it is recommended to use it only in the middle part of the country. Lack of castor alcohol mixture - high crystallization temperature of castor oil. Crystallization begins at –5 °C and proceeds intensively at –20 °C. As a result, clots form, which can clog the hydraulic drive lines and cause the vehicle's brakes to fail. BSK liquid is not recommended to be used at ambient air temperatures below –20 °C and above +30 °C. It should be protected from water, which can lead to delamination of the liquid. The liquid is used in the hydraulic brakes of old models of trucks and cars, except for VAZ cars.

**Brake fluid "Neva"** has a color from light yellow to yellow, transparent. It is recommended for cars. Its composition includes 51...59% ethyl carbitol, 31...34 - lyols, 5% carbitol ethers and 13.5% mixtures of glycols and polyglycols, as well as viscous and anti-corrosion additives. "Neva" liquid has good viscosity-temperature properties. Its density at 20 °C is 1012...1015 kg/m<sup>2</sup>, kinematic viscosity at 50 °C is not less than 5 sSt. It dissolves water well, the homogeneity of the water mixture is preserved at 40 °C and below. "Neva" brake fluid is flammable, its contact with human skin leads to dermatitis. The fluid is used in the hydraulic brake and clutch drive of old models of trucks and cars manufactured before 1985. The service life of the fluid does not exceed one year.

**Brake fluid "Tom"** was developed instead of "Neva" fluid and has better operational properties. It is made on the basis of ethylcarbolite and boron-containing polyester with the addition of thickening and anti-corrosion additives. It is fully compatible with Neva liquid, has good anti-corrosion and anti-wear properties and a slight decrease in the boiling point

when watering. "Tom" is operational at an ambient temperature of -40 °C to +45 °C. It is used in hydraulic brakes and clutches of all models of trucks and cars, with the exception of front-wheel drive VAZ cars. The service life of the liquid is two years. Foreign analogues of "Neva" and "Tom" fluids are brake fluids that meet the international DOT-3 classification.

**Brake fluids "Rosa DOT-4", "Rosa DOT-3", "Rosa-3" and "Rosa"** are high-temperature fluids produced on the basis of boron-containing polyester, and into which antioxidant and anti-corrosion additives are introduced. "Rosa" and "Rosa-3" brake fluids differ from "Rosa DOT-4" fluid only by the presence of various plasticizers in their composition. The liquid is usable at ambient temperatures from -40 °C to +45 °C. They are used in brake systems of modern cars and trucks. These fluids are compatible with "Tom" and "Neva" brake fluids in any ratio. The service life of liquids is three years.

### 13.3 DAMPING LIQUIDS

Shock absorbers serve to dampen body vibrations on elastic elements of the suspension. At the same time, the car runs smoothly even when driving on bad roads. **Damping liquids** are the working body in hydraulic shock absorbers of telescopic and lever-cam type.

The operation of the shock absorbers is based on the absorption of the kinetic energy of the vibration of the car body when the shock absorber fluid flows under pressure through narrow openings from one cavity to another. The fluid pressure in the shock absorbers is 8...11 MPa, and the temperature varies depending on the season and climatic conditions of the area from -50 °C to +140 °C. **Damping liquids should have good** viscosity-temperature, lubricating and antifoam properties, low solidification temperature, high antioxidative and mechanical stability, as well as compatibility with rubber seals.

The main operational indicator of shock absorber fluids **is viscosity** at positive and negative temperatures. At a temperature of -20 °C, the kinematic viscosity should not exceed 800 sSt. With a higher viscosity, the performance of the shock absorbers deteriorates significantly, the suspension is blocked.

Low-viscosity petroleum oils of various brands or their mixtures, which contain viscous, depressant, antioxidant, antiwear, dispersing and antifoam additives, are used as shock absorber fluids. The following shock-absorbing fluids are produced (table 13.3): AZh-12T, MGP-12 ("Slavol-AJ" trademark), GRZh-12.

Table 13.3 – Characteristics of shock absorber fluids

Indicator	AZh-12T	MGP-12	GRZh-12
Kinematic viscosity, mm <sup>2</sup> /s, at temperature:			
40°C, not less	—	—	16...20
50°C, not less	12	12	—
100°C, no less	3,6	3,8	3,9
-20°C, no more	—	800	800
-40°C, no more	6500	—	—

Continuation of table 13.3

Temperature, °C:			
flash, not lower	165	140	140
hardening, not higher	-52	-50	-50
Density at 20°C, mg/cm <sup>3</sup> , no more	—	917	917
Stability against oxidation:			
sediment after oxidation, %	unavailable	—	—
acid number before (after) oxidation, mg KOH/g, no more	0,04 (0,1)	—	—
The content of mechanical impurities and water, %	—	unavailable	unavailable
Corrosion test	endures		

**Damping liquid AZh-12T** is intended for telescopic and lever-cam shock absorbers of cars. The liquid is a mixture of low-viscosity oil of selective purification from sulfurous oils and ethyl polysiloxane liquid with anti-wear and antioxidant additives. Its kinematic viscosity at 50°C is not less than 12 mm<sup>2</sup>/s, at -40°C – not more than 6500 mm<sup>2</sup>/s; solidification temperature is -52°C, which ensures smooth operation of shock absorbers at any time of the year. Shock absorber liquid AJ-12G is transparent, from light yellow to light brown in color.

**Damping liquid MGP-12 ("Slavol-AZ")** is a low-viscosity, low-solidifying oil base, into which depressant, dispersant, anti-wear, antioxidant and anti-foam additives are introduced. Its kinematic viscosity at 50 °C is not less than 12 mm<sup>2</sup>/s, solidification temperature is not higher than -50 °C. The liquid is used in telescopic racks and shock absorbers of cars and trucks.

**Damping liquid GRZh-12** is a mixture of purified transformer and spindle distillates. Contains depressant, antioxidant, antiwear and antifoam additives. The kinematic viscosity at 40 °C is 10...20 mm<sup>2</sup>/s, the solidification temperature is -50 °C. The liquid is used in shock absorbers and telescopic racks of cars.

**Spindle oil AU (MG-22-A) and hydraulic oil AUP (MG-22-B)** are widely used for car shock absorbers, despite the fact that they have a high solidification temperature and unsatisfactory viscosity-temperature characteristics. Their viscosity increases rapidly with a decrease in temperature, in connection with which the stiffness of the shock absorbers increases.

A mixture of turbine and transformer oil in a ratio of approximately 1:1 is used for shock absorbers. However, it does not fully meet the requirements for shock absorber fluids. The mixture has a solidification temperature of about -30°C and insufficiently good viscosity-temperature characteristics. Kinematic viscosity at 50°C is 16...16.5 mm<sup>2</sup>/s.

### 13.4 STARTING LIQUIDS

Starting car engines at low temperatures is much more difficult. To facilitate the start of internal combustion engines in the cold season, two brands of starting fluids are used: "Kholod D-40" for diesel engines and "Arktika" for gasoline engines.

**Starting fluid "Kholod D-40"** is intended for diesel engines and has the following composition, %: ethyl ether - 58...62, isopropyl nitrate - 13...17, gas gasoline - 13...17 and low-viscosity oil - 8... 12. The main component of the starting fluid is ethyl ether, which has a low auto-ignition temperature, a wide flammability limit and a high saturated vapor pressure. Ethyl ether ensures self-ignition of the working mixture at relatively low temperatures (about 200°C). To ensure smooth and consistent ignition, isopropyl nitrate and gas gasoline are added to the mixture, which ignite after ethyl ether, but before the main fuel. To reduce the wear of parts when starting the engine, 8...12% oil is added to the composition of the starting fluid.

The liquid is released in sealed ampoules or in aerosol packaging (in metal cylinders). The liquid is injected into the diesel inlet pipe using the 6PP-40 starting device. Thanks to this, the start of a cold diesel engine is ensured at a normal ambient temperature of up to -40°C.

**Liquid "Arctic"** is used in those cases when pre-heating of the gasoline engine is impossible. The starting liquid has the following composition, %: ethyl ether - 45...60, gas gasoline - 35...55, ignition initiator (isopropyl nitrate) - 1.5, oil with an anti-seize additive - 2. The liquid is stored in ampoules or cylinders. It is introduced into the intake pipe of the engine using the starting device 6PP-40, after which it is possible to start a cold engine at ambient air temperatures of up to -40°C.

### **13.5 CONTROL QUESTIONS**

1. What requirements must coolants meet?
2. What are the composition and properties of low-freezing coolants?
3. What types of coolants do you know?
4. List the classes of antifreeze. How are they different?
5. What are brake fluids for?
6. List the brands of brake fluids.
7. What are shock absorber fluids for?
8. What properties should shock absorber fluids have?
9. List the brands of starting fluids.

## **LECTURE 14. CONSTRUCTION AND REPAIR MATERIALS (part 1)**

Lecture plan:

14.1 Paint and varnish materials.

14.2 Plastic materials.

14.3 Control questions.

### **14.1 PAINT AND VARNISH MATERIALS**

#### **Designation of paint and varnish materials**

Paints and varnishes serve to create a strong layer of varnishes and paints on the surface to be painted, preventing the formation of corrosion on car bodies (most often made of sheet steel) and body parts exposed to strong environmental influences such as weather conditions, road dirt, water, polluted air, mechanical abrasion, etc. and for decorative decoration.

Color is one of the indicators characterizing a passenger car. It creates not only a general impression: high-quality paint and subsequent systematic and thorough care of it is also reliable protection against corrosion, extending the service life of the car.

During the operation of cars, paint coatings lose their qualities. The top layer of the coating fades, loses its original color. Scratches, cracks and other defects appear that require restoration of the coating.

To maintain the good appearance of the car, constant care of the paint coating is necessary, as well as its partial or complete replacement.

#### **Requirements for paint and varnish coatings**

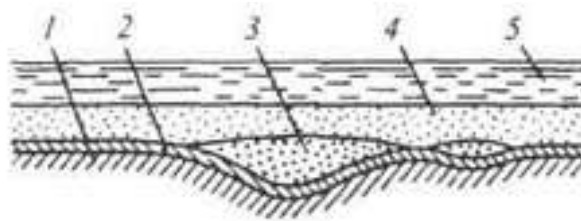
According to the purpose, paint and varnish materials and their coatings must meet the following basic requirements:

- stay firmly on the surface;
- have the necessary mechanical strength, hardness and elasticity;
- have resistance against the influence of moisture, oil products, exhaust gases and sunlight;
- be waterproof and gas-tight;
- retain their properties at positive temperatures in summer and negative temperatures in winter (have temperature resistance);
- be neutral, do not cause corrosion of painted surfaces;
- to dry quickly after application to the surface and not require complex drying devices for this;
- provide the required color of the painted surface with the minimum thickness and number of applied layers.
- have good coverage;
- the surface of the paint coating should be resistant to modern methods and means of washing and cleaning;
- have resistance to the influence of such factors as ultraviolet rays, exhaust gases and other aggressive products;
- be inexpensive, durable and allow for partial or full recovery in inexpensive and accessible ways.

None of the modern materials fully meet these requirements. For this and a number of other reasons, in most cases, coatings are made multi-layered, in which each of the layers or a group of them fully meets only one or several requirements. To improve the appearance of the car, paint coatings with "metallic" and mother-of-pearl effects, shiny, and two-tone coatings are increasingly used. The total number and quality of such narrowly functional layers is selected so that the coating as a whole meets the necessary extent of the totality of all requirements.

#### **Structure of paint coating and requirements for basic materials**

The main elements of the structure of a multi-layer paint coating (Fig. 14.1) are a layer of soil, a layer of putty and several layers of paint. These layers are applied in a certain technological sequence.



1 - surface to be painted; 2 - soil layer; 3 - a layer of local putty;  
4 - a layer of general putty; 5 - a layer of paint.

Figure 14.1 – Structure of multi-layer paint coating

Paint coatings are applied only to previously prepared surfaces from which dust, dirt, rust, scale, welding flux residues, films of petroleum products, grease stains that have become unsuitable for old coatings, etc., have been removed.

The first layer of coating - *soil* - is applied to the prepared surface. Its main purpose is to ensure high adhesion between metals and subsequent coating layers.

The dried soil has a small (about 15-30  $\mu\text{m}$ ) thickness, so dents, scratches and other defects are completely preserved on the primed product.

Based on this, soils are required to:

- high adhesion (adhesion) to metals, wood and other structural materials;
- the ability to hold the next layers of the coating in itself with the help of interpenetration of materials;
- good anti-corrosion properties;
- if possible, quick drying.

***Priming, filling and sealing of the surface*** to be painted is carried out with a number of primers produced by industry and available on the market. The choice of a certain type of priming depends on the treatment of a certain type of surface.

The following primers are produced:

- primer for pure metal;
- primer-pore filler;
- primer for protection against stone impacts;
- primer and pore filler for plastics;
- means of increasing adhesion, etc.

**Puttying** – is a process of filling pores, which serves to level the surface to be painted by filling existing recesses on it. There are local and general putty layers.

The first is aimed at leveling large defects, the second is at obtaining a smooth coating over the entire painted area.

Putty materials require:

- good adhesion to soils;
- sufficient mechanical strength, especially shock and vibration resistance;
- relatively good drying properties;
- the ability to grind.

The processed putty, and in its absence, the primed surface, is covered with several layers of paint, the number and processing of which depend on the requirements for the appearance of the coating, on the conditions of its operation, etc. With any painting method, each layer undergoes a drying stage, and the outer layers can be additionally sanded and polished.

Paints require:

- sufficient adhesion to soils and putties;
- the ability to form a continuous protective film;
- high weather resistance;
- resistance to the influence of technical fluids and other substances with which the coating comes into contact during the operation of machines;
- the ability to well cover the color of the lower layers of the coating;
- sufficient resistance to mechanical influences: impacts, vibration, bending, etc.;
- the ability to polish.

It should be noted that the technological processes of applying paint coatings at a car manufacturing plant and during car repair are significantly different from each other. As an example, Figure 14.2 shows the technological schemes of coating the car body with paint and varnish materials in factory conditions.

For a general high-quality repair system, the following materials are recommended:

- silicone remover;
- a two-component primer based on urethane;
- two-component polyester primer;
- a two-component urethane-based pore filler;
- two-component primer-pore filler for thick layer application;
- two-component coating enamel based on acrylic urethane;
- enamel base in a two-layer system;
- two-component transparent lacquer based on acrylic urethane.

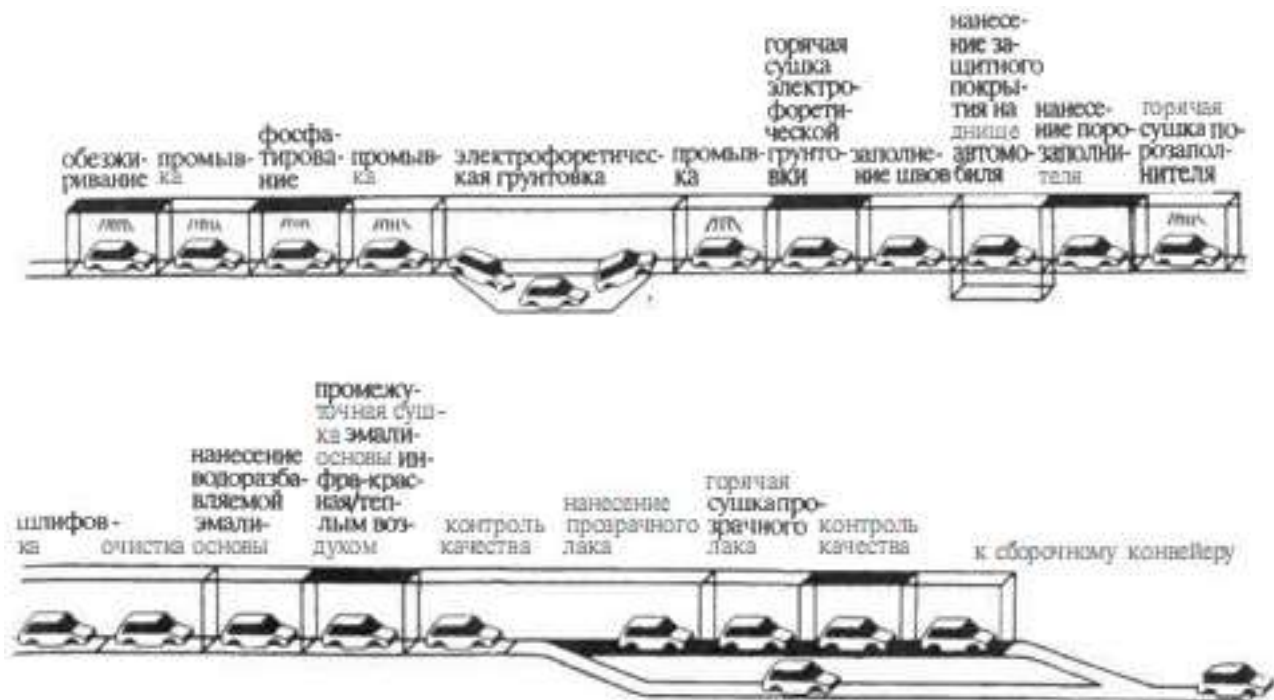


Figure 14.2 – Example of car body painting technology in factory conditions

When using the "wet on wet" paint system, it is recommended to use the following materials:

- silicone removal composition;
- two-component polyester putty;
- two-component soil-pore filler;
- two-component coating enamel based on acrylic urethane;
- enamel base in a two-layer system;
- two-component transparent lacquer based on acrylic urethane.

#### **Classification of designations of paint and varnish materials**

Paints and varnishes are divided into *basic and auxiliary* (GOST 9825-73). The main ones include soils, putties, varnishes and paints. Among the auxiliaries are liquids for preparing the surface for painting and caring for paint and varnish coatings.

***Paints and varnishes are indicated by five groups of signs.***

***The first group*** of signs defines the type of paint and varnish material and is indicated by a full word, for example, "primer", "putty", "enamel", "varnish".

***The second group*** of signs defines the main resin that is part of the film-forming substance and is denoted by two letters: GF – glyphthalic, PF – pentaphthalic, FL – phenolic, ML – melamine, EP – epoxy, PL – polyvinyl acetate, AC – copolymers NC – nitrocellulose, MA - vegetable oils, etc.

***The third group*** of signs defines the group to which the paint and varnish material is assigned according to its primary purpose: 0 – semi-finished primers and varnishes, 00 – putty, 1 – weatherproof, 2 – stable indoors, 5 – special (for leather, rubber, etc.), 7 – resistant to various environments, 8 – heat resistant, 9 – electrically insulating. A dash is placed between the second and third groups of signs.

***The fourth group*** of signs determines the serial number assigned to this paint and varnish material, and is indicated by one, two or three digits.

**The fifth group** of signs belongs mainly to enamels and determines their color. It is indicated entirely by words ("white", "blue", and if there are shades "blue-1", "blue-2", etc.). If the color of the enamel is given a number, then in the fifth group of signs the number of the color is indicated first, and then the color is written completely in words, while a dash is placed between the fourth and fifth groups of signs.

According to the above, it follows from the designation "ML-12-38 blue enamel" that the main film-forming melamine resin (ML) is in this enamel; enamel is weatherproof (1), its serial number is second (2), and its color is blue (38). According to the designation "Varnish GF-95", it can be established that this glyftal varnish (GF) is electrically insulating (9) and has the fifth serial number (5).

Paint coatings are classified by coating material, surface appearance (coating class) and operating conditions (coating group) (GOST 9.032-74).

The covering material is marked in accordance with the above.

**According to the appearance of the surface, paint coatings are divided into four classes.**

**The first class** is characterized by a flat, single-toned surface, without defects visible to the naked eye. According to the first class, car bodies are painted, and in this case, the paint coating consists of soil, local and general putty, and 3-6 layers of paint. The coating surface is thoroughly polished.

**The second class** allows some inconspicuous defects on the surface: dust, scratches, traces of cleaning, etc. According to the second class, bus bodies, cabins, wings and hoods of trucks, tractors, construction and road vehicles are painted. Second class coatings usually include soil, local putty and 2-4 coats of paint.

**The third class** allows for irregularities related to the condition of the surface to be painted before it is painted.

**The fourth class** allows visible defects that affect the protective properties of the coating. According to the third and fourth class, frames, axles, wheels, loading platforms, working bodies and other parts of machines that only need anti-corrosion protection are painted. Coatings of the third and fourth class usually consist of soil and 1-2 layers of paint. In some cases, coatings of the fourth class consist of a single layer of paint.

**According to the conditions** of operation (stability), paint coatings are divided into eight groups: stable indoors (P); weatherproof (A), which include coatings for cars, tractors, construction and road vehicles; chemically resistant (X, XK, XIII); waterproof in fresh (B) and sea water (BM); heat-resistant (T); oil-resistant (M); gasoline-resistant (B) and electrically insulating (E).

**According to the degree of gloss**, paint coatings are divided into glossy, semi-gloss and matte. The degree of gloss is characterized by the coating material.

For example, the designation "EM NC-25, blue, 1.P" indicates that the paint coating is applied with blue nitroenamel (NC), made according to the first class (1) and stable during indoor use (P).

The highest requirements for paint coatings are made when painting the bodies of passenger cars and buses. Here, in addition to other requirements, it is very important that the coating has a good appearance. These coatings consist of a primer, local and general putty and several (2-5) layers of paint.

Covering trucks consists of a primer, local putty and 1-2 layers of paint.

Car units (engines, frames, wheels, etc.), as well as wooden cargo platforms, are covered with one layer of soil (not always) and 1-2 layers of paint.

The total thickness of the paint coating usually does not exceed 0.1 mm.

The leading European manufacturers of repair paint and varnish materials have created a symbolic language that is understandable to everyone - the icons found on the packages of paint and varnish materials of many companies. Figure 14.3 shows the icons and their meanings.

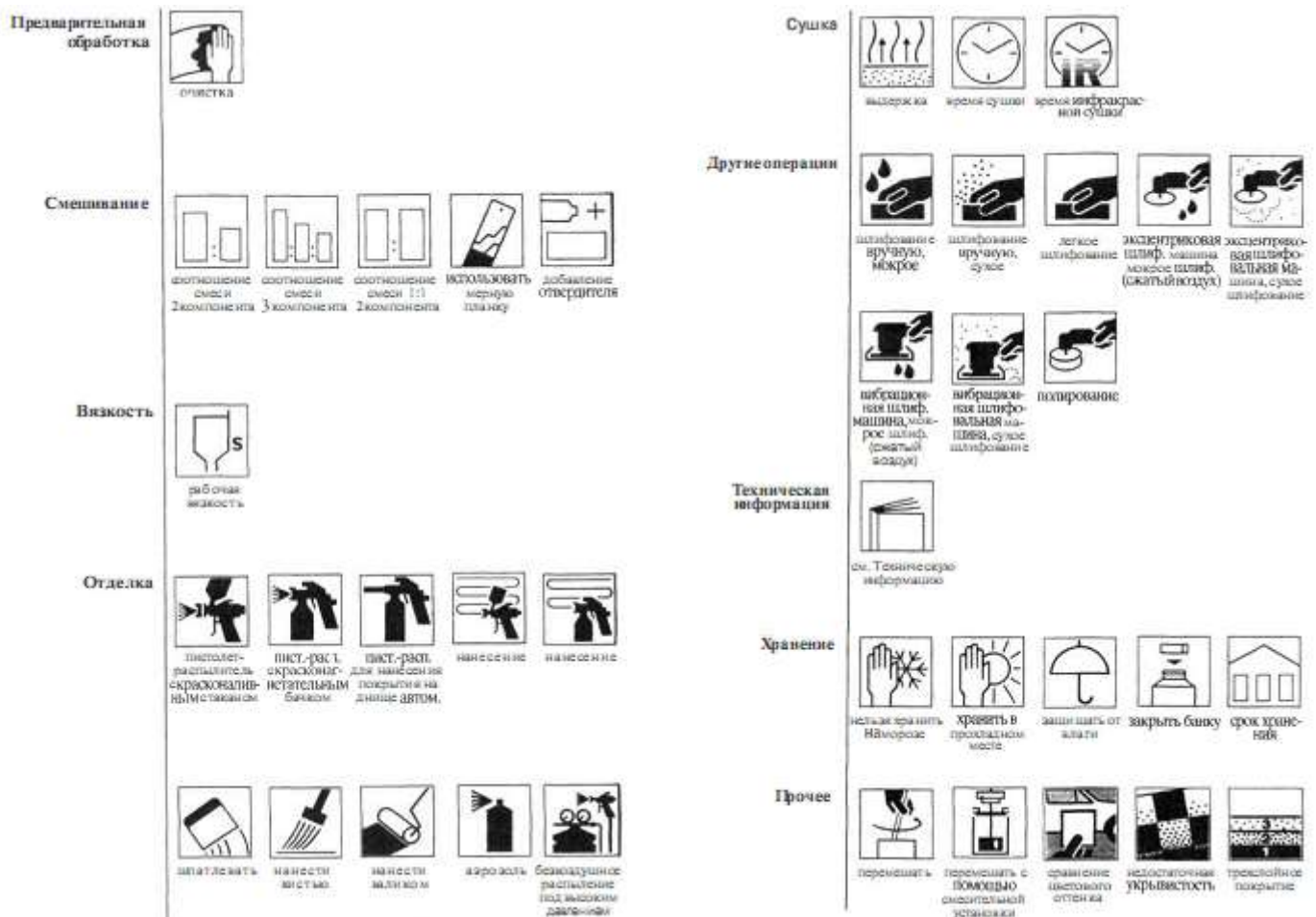


Figure 14.3 – Icons and their meanings

### **Paint materials used in repair painting**

You need to remember the following:

- compatibility of all components of paint and varnish materials is achieved only if materials of the same manufacturer (firm) are used;
- follow the manufacturer's recommendations. It is important to make the correct selection of hardener, thinner (certain mixture ratio) for the climatic conditions in which the material will be used.

**Removal of paint and varnish materials.** There are two ways to remove the lacquer coating from the surface:

- with the help of various grinding machines;
- using solvents (chemical removal).

**Puttying-pore filling.** Two-component polyester putty is most often used for puttying. First, the surface must be degreased, rust must be removed from it, and then it must be dried.

Two-component polyester putties have good adhesive properties with all surfaces (pure metal, primers, paint layers in good condition). Now there are universal polyester putties that can be applied to galvanized steel surfaces.

**Priming, filling and sealing.** A whole range of primers is produced. The selection of the primer depends on the respective task and the type of coating enamel.

Primer for pure metal. If a clean metal appears after preliminary preparation of the surface, then a one-component anti-corrosion primer is applied to it, which, thanks to the special composition of pigments and resins, has good anti-corrosion and adhesive properties. This primer can also be used to apply it to parts made of aluminum, pure steel or galvanized.

**Pore-filling soils.** Currently, two-component materials based on acrylic polyurethane are used. They have good adhesive properties, require a short drying time and are easy to sand.

Two types of soil-pore fillers are produced. The first is used to perform high-quality work during full painting of the car body. It has high resistance, good insulating and adhesive properties. The second primer can be applied by the "wet on wet" method, and at the same time, the durability of the paint and varnish material is in the range from normal to medium with very good pouring and good insulating properties; easily sanded.

**Primers for protection against stone impacts.** These are most often water-diluted products that can be applied to a two-component soil-pore filler. They can be unpainted or painted with topcoats based on synthetic resin or two-component acrylic topcoats.

**Adhesion-enhancing agents** are used to strengthen the adhesion between the old and new paintwork, as well as as an insulating layer to prevent damage to the coating materials.

**Primers and fillers for plastics.** Many different types of plastics are currently used in cars. Special means of increasing the adhesion of plastics are produced. Two-component pore-filling soils modified with plasticizers are applied to them.

**Application of coating materials.** Coating enamels are the main element of paint coating.

One of the four constituent elements of enamel is resin, which depends on the possibility of applying it to the surface, drying, ability to be repainted, and hardness.

The resins currently contained in repair paint materials are divided into: nitrocellulose, synthetic alkynes, acrylic.

**Nitrocellulose resins.** Used since the 60s, they are made from wood fiber and cotton waste. This resin is a polymer material that requires a large amount of solvent to reduce viscosity and obtain a finished material. Nitrocellulose enamels have low weather resistance, are characterized by fast drying (rapid evaporation of solvents), ease of application and polishing, and are easily repainted.

**Synthetic resins.** Synthetic resins can be used for several years. The name "synthetic resin" can refer to many different materials. Metal catalysts or accelerators are often added to speed up drying. Synthetic resins contain fewer solvents than nitrocellulose and therefore a thicker film is formed on the surface to be painted. They dry slowly.

**Acrylic resins.** They are divided into two groups - one-component acrylic resin (thermoplastic) and two-component acrylic resin.

**One-component acrylic resins.** They dry quickly, like nitrocellulose, but are less exposed to sunlight - less likely to fade. They form a very thin film on the surface, are very fragile, and are difficult to repaint.

**Two-component acrylic resins.** They are made of two components - oxyacrylic resin and isocyanate-based hardener. After mixing these components, the enamel dries even at room temperature. Since two-component acrylic resins contain a small amount of solvents, when they are completely hardened, a film thicker than one layer is formed. In terms of their properties, they are close to factory paint coatings (they have high chemical resistance, ability to be repainted, elasticity, hardness).

### **Components of paint and varnish materials**

Paint and paint materials, from which paint and paint coatings are obtained, have a liquid consistency and contain many components.

The main mass of varnishes is not used in its pure form, but goes along with oil for the preparation of paints, primers and other materials. For this purpose, a pigment is introduced into the varnish or oil. Depending on the type of film former, two types of paints are obtained:

oil + pigment → oil paint;

varnish+pigment → enamel paint.

**Pigments.** Powdered metal oxides (iron, lead, zinc, titanium, etc.), some carefully ground natural inorganic substances (chalk, ocher) and aluminum powder became the most widely used pigments. The main purpose of pigments is to give paint the desired color. Unlike dyes, they are insoluble in varnishes and oil and therefore must be maintained in a suspended state during painting. In other words, oil and enamel paints are a suspension, and this fact is reflected in the properties of the coating. When the paint applied to the product dries, the pigments suspended in it are packaged in a certain way, which increases the strength of the coating, increases weather resistance, reduces flammability, etc.

**Film formers.** The basis of varnishes, paints, primers and putties are film formers - solid or liquid substances capable of creating a continuous solid covering film. The strength of the connection between the paint coating and the surface to be painted, the resistance against the influence of the external environment (primarily against the influence of corrosion) and other important qualities of the coatings depend on the film formers. Liquid and solid film formers are used.

**Liquid film formers** include natural and synthetic drying oils (linseed, hemp, cottonseed, sunflower, etc.), on the basis of which oil varnishes and paints, oil primers and putties are prepared. In the form of thermally and chemically processed products, they are the basis of various types of olive oil. The best varieties of olive oil (natural) are obtained from linseed oil.

**Solid film formers** are natural resins (shellac, rosin and its processing products, asphalt, etc.) and synthetic thermoplastic, thermoreactive, and curing polymers (glyphthalic and resole resins, ethers, cellulose, etc.). To strengthen certain properties of film-forming agents, they are often obtained in the form of a mixture. For example, oil-resin film formers consisting of resins and oils are used in the production of common glyphthalic and pentaphthalic enamel paints.

The process of forming paint coatings for different film formers proceeds differently. Film formers, in which chemical transformations do not occur during drying, are called **non-convertible**, and the coatings obtained from them are called **reversible**. All thermoplastic polymers will belong to this group of film-forming substances. The drying time of paints containing non-convertible film formers will be determined by the volatility of the solvent and the thickness of the film.

Film formers capable of undergoing chemical transformations during the drying process are called **transformable**. In this case, unsaturated resins and oils or thermoreactive polymers serve as film formers. Drying of the material, in addition to evaporation of the solvent, is accompanied by polymerization, polycondensation and oxidation reactions with the formation of coatings with a spatial structure of macromolecules. In order to accelerate the drying and strengthening of paint coatings in these cases, an elevated temperature (hot drying) or the introduction of appropriate catalysts (siccatives) into the paint is required. The resulting coating is irreversible and cannot be turned back into a liquid by treatment with a solvent.

**Solvents.** Solvents serve to dissolve film formers and form varnishes. They are volatile liquid organic compounds that must evaporate without a residue after applying the paint material to the surface.

**Thinners.** Thinners are used to partially replace the solvent and to reduce the viscosity of paint materials, they are mixtures of cheaper products than solvents. The thinner in its pure form, as a rule, is not capable of dissolving film-formers, but, being added to varnish or other paint and varnish material, reduces its viscosity. An excess of thinner can cause the film-former to collapse and settle. When choosing thinners, it is necessary to take into account that the solvent has a lower volatility than the thinner.

The most widely used solvents and thinners include the following products:

- gasoline-solvent (white spirit) is a narrow fraction of direct distillation gasoline that boils in the range of 165...200°C;
- coal solvent (petroleum solvent) is a product of coal tar distillation and is a mixture of various aromatic hydrocarbons (xylene, toluene, benzene) and hydrocarbons of other groups;
- turpentine is a product of the distillation of the resin of coniferous trees. It is a transparent volatile liquid with a characteristic smell, without sediment and water. It boils at a temperature of no more than 153...170°C;
- coal xylene is an aromatic hydrocarbon obtained during the rectification of crude benzene;
- solvents №646, 647, 648, 650 and RDV thinner are mixtures of acetone, acetates, alcohols and aromatic hydrocarbons taken in different ratios.

**Plasticizers.** Plasticizers, or softeners, can be added to nitrocellulose paint materials to give the coating flexibility. They can also increase adhesion, light, heat and frost resistance. Liquid and solid non-volatile organic products are used as plasticizers: tricresyl phosphate, triphenyl phosphate, camphor, castor and other vegetable oils and thermoplastic polymers. Due to the decrease in the content of the plasticizer, the fragility of the coating and its ability to break increase over time.

**Siccatives.** Siccating agents are substances that accelerate the process of formation of

a varnish oil film. They are oxides of lead, manganese, cobalt or salts of organic acids of these metals. Sicativs are used in liquid and solid form and are added to paints containing oil in certain quantities; large amounts of driers cause not a reduction, but an increase in drying time. Thanks to the catalytic effect of driers on the oxidation reaction and polymerization of the film, it hardens several times faster.

**Fillers.** Fillers are used as admixtures for too saturated and crooked dyes and their better fixing. The most common fillers are: inert - chalk, gypsum, kaolin, talc and active - aluminum oxide hydrate, blafix.

### **Properties of varnishes and paints**

The most important indicators of varnishes and paints include: viscosity, pouring, drying time, coverage, adhesion, strength and hardness of the film, water and oil and gasoline resistance, toxicity and fire hazard.

**Viscosity.** The optimal value of viscosity depends on the type of paint, and must also correspond to the selected method of its application. In most cases, viscosity fluctuations at 18...20 °C are within the following limits: for the immersion method, 15...20 s, spray application 20...30 s, and when painting with a brush, 30...60 s.

With increased viscosity, the thickness of the film of one layer increases and the strength of the film decreases, with reduced viscosity, the thickness of the film layer decreases and the solvent consumption increases.

**Pouring.** Pouring is the ability of paints to give an even, smooth surface, without brush strokes and without shagreen when applied with a sprayer. Pouring is considered satisfactory if traces of application disappear no later than 10 minutes after applying paint and varnish materials to the surface.

**Drying time.** The drying time of the paint and varnish material at a given temperature is measured in minutes until a thin film is formed on the surface - the so-called drying from dust: or until the complete evaporation of the solvent - complete drying. The duration of drying depends on the nature of the material and the air temperature. Seven degrees of drying are set: drying to the first degree corresponds to the so-called drying "from dust", to the third degree to complete drying, etc. A special method of determining this indicator has been developed. Nitro enamels are the fastest drying. The complete drying time at 18...20°C is 15...20 minutes. Due to this property, nitroenamel is widely used in repair practice.

**Coverage.** Opacity is the ability of paint to make the color of the surface to be painted invisible when applied in a thin, uniform layer. The coverage depends on the quantity and quality of the pigments introduced into the paint and on the properties of the film former. The paint consumption is judged by the coverage index: the lower the coverage index, the less paint consumption.

**Adhesion.** Adhesion is the ability of the paint film to stick to the surface being painted.

**Impact strength.** Impact strength is the ability of a film not to break under the action of an impact load.

**Bending strength.** The bending strength of the paint coating is characterized by the minimum diameter of the rod (20, 15, 10, 5, 3 and 1 mm), the bending of the coating at which the coloring of the metal film does not cause its mechanical destruction.

***Tensile strength.*** Tensile strength is measured in millimeters of the depth of the deflection of the metal plate at the moment of destruction of the applied coating film.

***Film hardness.*** The hardness of the film is expressed by the ratio of the damping time of the oscillations of the pendulum mounted on the surface of the film to the damping time of the oscillations of the same pendulum mounted on the glass plate.

***Gasoline and oil resistance.*** Gasoline and oil resistance is the ability of paint coatings to stay in gasoline or oil for a certain time at a given temperature without visible changes in the state of the film: peeling, appearance of wrinkles and bubbles.

***Toxicity and flammability.*** Paint and paint materials are mostly toxic, flammable and explosive substances.

Methods for determining the resistance of coatings to water, loss of gloss during wet irradiation, resistance of coatings to changes in temperature have been established.

Increasing requirements for the design of cars under the conditions of reducing energy costs in production and operation leads to the intensification of work aimed at increasing the use of plastics. The role of the latter in the automotive industry is constantly growing.

#### **Materials for preservation and care of paint coatings**

Effects of heat, light, air oxygen, moisture, and other chemical agents are factors for the destruction of paint coatings. In atmospheric conditions, the coating is subject to the complex influence of many factors. Coatings also deteriorate from vibration, impacts and other mechanical damage.

The energy of chemical bonds in the polymer from which it is formed has a decisive influence on the heat resistance of the coating.

The very components of the paint coating – pigments, plasticizers and other additives – have a significant impact on aging.

If pigments are catalysts or initiators of chemical processes, the destruction of the coating is accelerated. In the presence of pigments characterized by reflective properties or performing the functions of heat stabilizers, the destruction process slows down.

Increased destruction in many cases is caused by the presence of plasticizers and residual solvents in the film.

Weathering, sweating and leaching of the plasticizer increases the fragility of the coating, and the evaporation of residual solvents leads to its shrinkage and cracking.

Ultraviolet rays of sunlight have a strong destructive effect on the coating. In the presence of oxygen in the air, as well as when the temperature rises, the destruction accelerates and becomes more complicated: the mass of the film material decreases, various oxidation products are formed.

***Atmospheric aging of coatings*** is understood as a complex effect of solar radiation, moisture, air oxygen, changing temperatures, etc. It has been established that under atmospheric conditions paint coatings are destroyed 50 times faster than indoors. Under the influence of direct sunlight, the loss of gloss of coatings is several times greater than under the influence of diffused sunlight.

The aging process reaches its greatest destructive power with increasing intensity of solar radiation, air humidity and wind speed. Therefore, the gloss of coatings is lost most quickly in the spring and summer period.

Ionizing radiation, the result of which is the destruction and crosslinking of molecular chains, has a particularly strong effect on the paint coating. For example, polyisobutylene can turn into a liquid if the absorbed radiation dose was high enough.

Color change - discoloration, darkening, loss of gloss, appearance of bubbles, cracks and stickiness, flaking - signs of destruction of coatings under the influence of ionizing radiation.

Premature destruction of the coating occurs, in particular, due to its contamination, so the car body must be washed regularly, while avoiding the ingress of solid particles of dust and dirt that can scratch the enamel film.

***Washing the body with hot water causes rapid destruction of the paint coating.*** Rapid darkening and destruction of the coating also occurs if soda, washing powders and other alkaline solutions are used to wash the painted surface of the car.

Plaque, which is difficult to wash off with water, formed during the operation of the car, as well as point spots of brown color, resembling points of corrosion, are removed by washing the body with warm soapy water (50 g of soap shavings or neutral soap per one bucket of water). The paint coating can be periodically washed with aqueous solutions of special car shampoos.

There are several types of car body protection:

- passive – isolation of the surface from atmospheric influence;
- active – when the protective agent forms a resistant layer against corrosion on the surface of the metal;
- transforming – the transfer of already oxidized metal into a film resistant to the effects of oxygen, moisture and soluble salts.

***Passive*** means of protection include mastics for protecting the bottom of the body. Mastic differs from paint in that it is prepared on a bitumen, rubber, resin base, and may include graphite, fibrous substances, and oils. Mastic is applied to a dry, cleaned surface in a thick layer. This ensures the resistance of the coating to the mechanical effects of sand and gravel flying from under the wheels; noise reduction due to damping effect. The mastic protects only the open surfaces of the bottom, it does not get into the cracks.

Passive protection is useless if the surface has not been previously cleaned of dirt and water, because in this case electrochemical corrosion occurs.

Among ***the active*** corrosion protection agents, we should mention "Movil", developed on the basis of the American drug "Tectile 309AW" of the company "Valvoline". "Movil" not only physically isolates the surface of the metal from air and moisture, but thanks to the corrosion inhibitor contained in it, actively fights against rusting. Moreover, it has a high surface tension, thanks to which it gets into narrow gaps and is even able to displace water from the surface.

***Converting*** compounds include compounds that turn rust into soil. They are prepared on the basis of orthophosphoric acid. These preparations are an effective means of combating corrosion that has already begun. A surface covered with rust, treated with such a preparation, can be painted without additional treatment.

One of the progressive directions of the development of automotive chemistry is the so-called auto cosmetics. Car cosmetics products include polishes, car shampoos, means for removing various stains, for cleaning glass and coatings, etc. Every year, the number and quality of various car cosmetics products increases.

The coating, which has lost its original appearance, is recommended to be periodically polished to restore its shine. This process helps to clean the surface, remove small cracks invisible to the eye, and gives the coating an even and shiny appearance. All this protects it from further destruction.

**For polishing** paint coatings, use: polishing water (suspension of soft abrasives with binders); wax polishing pastes (for example, a mixture of wax, paraffin, kerosene or turpentine, white spirit); liquid polishing compositions (for example, a mixture of white carbon black - aluminum oxide and wax-containing emulsion); polishing pastes (mixture of fine abrasives, oils, household soap and solvent). To remove deep cracks, the coating is first treated with a grinding paste consisting of a hard abrasive (for example, Alund powder), paraffin and oil (for example, petroleum jelly), and then polished. Defects in coatings made of melamine alkyd enamels are eliminated with grinding paste, which is a suspension of alumina in a mixture of oils, solvents and water. Grinding paste allows you to remove a layer of coatings that has cracks, 15...20 microns thick.

The mechanism of action of polishing compositions or pastes is as follows: grinding and polishing are performed with abrasives, wax fills the pores of the film and smoothes out microscopic irregularities, solvents remove the remains of grease stains and other impurities.

Auto polishes form a strong, shiny, protective film on the surface of the paint coating. They differ mainly in stability and the method of application to the surface. Car polishes in an aerosol package are easier to apply and rub than ordinary ones, they are used more economically, but cars need to be treated with them 4-5 times more often. They are stored on the surface of the body for 2-3 weeks or until the first washing with shampoo. Preservative polish preserves the protective film for 2-12 months.

Auto cosmetic products also include car shampoos. Car shampoos consist of a concentrated solution or granules from a mixture of soluble and detergent substances that are prone to biodegradation (more environmentally friendly). Currently, preparations are produced that combine the properties of shampoo and polish. Since there is a large number of decorative and finishing materials in the car, various cleaning products are produced to care for them.

Means for cleaning and washing the windshield and car optics are produced. Preparations for car glass are divided into liquids used in the washer tank (low-freezing) and used as protective (water-repellent) coatings. To prevent fogging and icing of the car glass, drugs are produced in aerosol packaging and in the form of napkins.

Caring and caring for your car can significantly extend its life.

## **14.2 PLASTIC MATERIALS**

### **Purpose of plastics**

The improvement of the car design is associated with the constant expansion of the use of various types of plastics as structural materials.

In the automotive industry, the volume of use of plastics as structural materials is steadily increasing. Various compositions of polyethylene, polypropylene, their block copolymer, as well as polyamides and polyurethane foam are most widely used.

Plastic masses refer to polymeric high-molecular synthetic materials. They can be welded, pressed and rolled like metal. They can be used to cast parts of the most complex shape.

The use of such plastics as polyethylene, copolymer of ethylene with vinyl acetate, polypropylene, polyamide, polycarbonate is growing at the fastest rate. A sharp increase in the use of plastics for the manufacture of body parts is expected.

Plastics are used to make bumpers, door structures, trunks, and hoods. An almost complete transition to plastic fuel tanks is planned.

The use of plastics affects the total weight of the car, and therefore reduces the load on the axle, fuel economy, traction-dynamic indicators and competitiveness. It is also very important that plastics save expensive and scarce non-ferrous metals. A typical example is the replacement of metal pipelines of braking systems with polyamide ones. Currently, the introduction of plastics continues at the KrAZ enterprise - the production of multi-layer parts for the interior upholstery of car cabins, as well as large-sized parts of the outer belt of the cabin (bumper, cladding, wings, footrests, etc.) is being organized.

A composition based on polyethylene is used for the manufacture of car fuel tanks; polyolefin compositions are used for the production of mudguards and mats - pallets. Instrument panels, console, steering column casing, key switch panel, lamp housings, lampshades and instruments are made of polypropylene compositions with mineral fillers and various reinforcing modifiers.

The general positive technical and economic qualities of plastic masses include the following:

- the lower cost of plastic products compared to the cost of products made of metals or other materials;
- low density, as a rule, not exceeding  $1500 \text{ kg/m}^3$ , which is approximately 5-8 times lower than that of steel;
- a high strength-to-density ratio, i.e. significant specific volume strength;
- good electrical, heat and sound insulation properties;
- easy processing into products, which indicates high manufacturability;
- high resistance to various aggressive environments;
- the possibility of providing pronounced anti-friction or pronounced frictional properties;
- good transparency and ability to be dyed;
- resistance to vibrations.

In general, the use of plastics in the automotive industry provides:

- reducing the material consumption of structures due to the use of large-sized and other parts;
- increased safety due to the use of semi-rigid, elastic polyurethane foam for seats, steering wheels, armrests, ceiling, instrument panels, bumpers and other parts;
- increase in durability due to the use of coatings of parts facing the road surface, the use of wings, aprons, bumpers and other plastic parts;
- reduction of labor intensity due to the high technological flexibility of plastics when processing them into products.

Thus, by replacing ferrous metals with cast plastics, they achieve a reduction in the labor intensity of manufacturing parts by approximately 5-6 times.

A characteristic feature of plastics is that depending on the components used for their production, the ratio of these components and the technological regime, materials with pronounced properties can be obtained.

Plastic coatings give products a good appearance, and they also reliably protect metal from corrosion, due to which 8-10% of all metal produced in the CIS countries fails annually.

### Composition of plastics

Materials that contain a polymer as the main binding component are called **plastics**.

Plastics are diverse in their composition. In general, they include polymers, fillers, plasticizers, antioxidants, and dyes. Depending on the type of plastic, its composition includes all the listed components or only some of them. There are rare cases when products are made of only one polymer, and then the concepts of plastic and polymer become identical.

**Polymer.** Polymer is the main element of plastic, which acts as a binder. Polymer compounds can be synthetic (polyethylene, phenol-formaldehyde resins, etc.) and natural (natural rubber, cellulose, resins, etc.).

A characteristic feature of both synthetic and natural polymers is plasticity, the ability of the material to take the shape given to it under the influence of heat and pressure and to keep it stably.

Macromolecules with a linear structure are formed during a polymerization reaction, when several identical molecules are joined together without the release of byproducts. Both the same monomers and different monomers in the amount of 2-3 or more can enter the polymerization reaction. Such complex polymers are called copolymers. Schemes of the structure of the specified types of polymers are shown in Figure 14.4.



*A and B are different links of macromolecules*

Figure 14.4 – Structure diagrams of polymers

According to their properties, polymers are divided into **thermoplastic** (plastics based on them belong to the group of thermoplastics) and **thermosetting** (plastics based on them belong to the group of thermosetting). Some plastics contain both thermosetting and thermoplastic polymers.

To improve the properties of plastics, the following additives are introduced into them - fillers, antioxidants, dyes.

**Fillers.** Fillers serve to increase the volume and improve the physico-mechanical and other properties of plastics, as well as to reduce shrinkage during the hardening of plastics, which in some cases reaches 10-20% by volume. Wood flour, quartz or asbestos powder, cotton lint, glass fibers are used as fillers. To obtain particularly strong plastics, cotton and glass fabrics, paper or wood veneer (a thin sheet of wood) are used as a filler. Such plastics are called layered plastics.

**Plasticizers.** Plasticizers serve to reduce the brittleness of plastics. These include liquids (dibutyl phthalate, dioctyl phthalate, etc.) or low-melting waxy substances that are well combined with polymers. The fragility of the plastic decreases as a result of the penetration of the plasticizer into the interchain space of the polymer.

**Antioxidants.** Antioxidants (antioxidants) slow down the oxidation process of plastics during their use, especially at elevated temperatures and exposure to light.

**Dyes.** Dyes serve to give plastics the necessary decorative appearance, as well as to reduce moisture and light absorption.

In addition, stabilizers are introduced into plastics, which bind low-molecular products of polymer decomposition; accelerators or retarders of the process of solidification of plastics, as well as lubricants that prevent plastics from sticking to the walls of the mold.

The low density of plastics allows to reduce the mass of manufactured parts. Since the strength of plastics decreases with increasing temperature, plastics are often reinforced with metal.

### Classification of plastics

*Plastic masses, depending on the chemical nature of the polymers, are divided into four classes.*

**Class A.** Plastic masses based on high-molecular compounds obtained by chain polymerization: polyethylene VD, polyethylene ND, propylene, vinyl plastic and plastics based on polyvinyl chloride; polyisobutylene; fluoroplastics; polystyrene and its copolymers; ethinoplasts (polyvinylbutyrol, etc.), acryloplasts, etc.

**Class B.** Plastic masses based on polymers obtained by polycondensation and stepwise polymerization: phenoplasts with various fillers (press powders, fibers, textolites, glass fibers, phalloid, etc.); aminoplasts; melalith; etheroplasts; polyamides (kapron, etc.); urethane plastics; epoxy resins, etc.

**Class C.** Plastic masses based on chemically modified natural polymers. These include plastic masses based on cellulose derivatives (celluloid, etrols), halalite.

**Class D.** Plastic masses based on natural and petroleum asphalts and resins: bituminous plastics with various fillers. In addition to this classification, plastics are divided into two main groups - thermoset and thermoplastic and into subgroups according to physical and mechanical properties.

### Properties of plastics

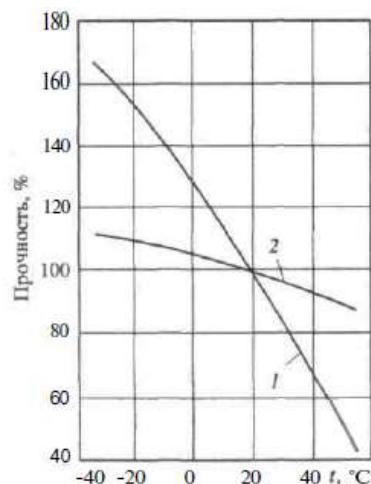
**Density.** The density of most plastics is 900-2200 kg/m<sup>3</sup>. Low density is one of the advantages of plastics over other materials, which allows you to reduce the weight of the product.

**Strength.** Unlike metals, the strength properties of plastics depend on the shape and size of the product, and on the time of use. A characteristic feature of plastics is their ability to change dimensions under constant load.

After prolonged exposure to constant load, the strength of plastics decreases. As a result, plastics are not suitable where they are subjected to constant (albeit permissible) loads during operation. At the same time, due to their elasticity, plastics withstand variable loads better than metal.

The working temperature range of plastics is much narrower than that of steels. And the influence of temperature within this interval on the dimensions of parts and strength

properties of plastics is much higher (Fig. 14.5).



1 - thermoplastics; 2 - reactive plastics

Figure 14.5 – Dependence of plastic strength on temperature

The magnitudes of strength limits and modulus of elasticity of plastics are significantly smaller than those of steels. Therefore, plastics are not suitable where high rigidity of products is required. To increase rigidity, plastic parts are sometimes reinforced with metal.

The strongest plastic is fiberglass, the tensile strength of which reaches 70 kg/mm<sup>2</sup>.

**Heat resistance.** Most plastics can work in the following temperature range:

- thermoplastics from –50°C to +80°C,
- reactive plastics up to +120°C.

Plastics based on organosilicon polymers and fluoroplastics work at temperatures up to +500°C. Most plastics undergo destruction at temperatures of 250-350°C, that is, the process of decomposition of the polymer into monomers and other substances (water, carbon dioxide, aldehydes, etc.). Insufficient heat resistance is the main disadvantage of plastics as structural materials.

**Frost resistance.** Frost resistance demonstrates the nature of changes in the mechanical properties of plastics in the region of negative temperatures. Most plastics at negative temperatures, especially thermoplastics, lose their plasticity and become brittle.

**Thermal conductivity.** Plastics have much lower thermal conductivity than metals, which have 500-600 times higher thermal conductivity.

**Optical characteristics.** Organic glass, a colorless, transparent plastic, transmits ultraviolet rays particularly well compared to silicate glass.

**Corrosion resistance.** As a rule, plastic masses, unlike metals, have increased resistance to the effects of acids, alkalis, salts and solvents.

**Dielectric properties.** Plastic masses refer to dielectrics.

**Frictional properties.** Layered plastics (kapron) are characterized by a low coefficient of friction and high wear resistance, so they are used in bearings and other friction components. Plastics based on phenolic resins with asbestos filler - asbestos fibers, have a high coefficient of friction and are used in braking devices.

**Resistance to atmospheric influences.** Plastics change their properties under the influence of moisture, light and water.

**The main reason** for the aging of plastics is the destruction of polymers under the influence of sunlight and heat, as well as the simultaneous processes of oxidation of polymers. The relative ephemerality of plastics is their serious disadvantage compared to metal and calls for measures to prevent aging.

### **Thermoplastic plastics**

Thermoplastic polymer compounds acquire plasticity when heated, return to a solid state when cooled, melt again and again without changing the properties of the material. They include all plastics of class "A" and partly of class "B" (polystyrene, polyethylene, vinyl plastic, etc.).

Thermoplastic plastics (thermoplastics) are obtained by polymerization of low molecular weight organic substances. Thermoplastics are available with or without filler. To improve anti-friction properties, increase thermal conductivity, wear resistance of polyamides and fluoroplastics, fillers are introduced: graphite, ground coke, lead, bronze, molybdenum disulfide, glass fiber, etc.

Unfilled commercial thermoplastics are plasticized and non-plasticized. Various synthetic organic and inorganic substances are used as stabilizers and antiaging agents. Moreover, each polymer is stabilized by certain substances.

Most thermoplastics have high impact strength, water resistance and good dielectric properties, and at the same time low heat resistance and significant cold flow. Therefore, many thermoplastic plastics can be used at a temperature not higher than 60...80°C. For some of these plastics, it can reach 150...160 and even 250°C (for example, for fluoroplastic). Thermoplastic plastics (especially fluoroplastics) are prone to significant changes in linear dimensions and volume with temperature changes.

Among plastics based on thermoplastic resins, polyamides, acryloplasts (polymethyl methacrylate), polyvinyl chloride (vinyl plastics), fluoroplastics, polyethylene, polystyrene, etrols (thermoplastic cellulose ethers) have received the most widespread use in the automotive industry.

**Polyamides**, including kapron (polycaprolactam), can be made of a large number of various automotive parts: bushings (pedals, door hinges, springs, etc.), bearings (bus doors, clutch pedals, etc.), liners, oil seal housings, gears (speedometer drive, etc.), cuffs, glass holders, lamp sockets, switches, etc.

**Covers**, buttons, lighting shades, tubes, gaskets and other parts are made from HD polyethylene, as well as a film based on which drapery and upholstery fabrics for seats and backs are obtained.

**Polyvinyl chloride (vinylplast)** is used for the manufacture of battery cans, gaskets, seals, and body lining. Plasticized polyvinyl chloride is used to produce upholstery materials by applying a film to cotton fabric, making oil and fuel pipes and other parts.

**Fluoroplastics** are used for parts that work in chemical environments and at elevated temperatures.

**Acryloplasts** are used to make dust-proof lenses, internal lampshades, sidelight glasses, windows and other details.

**From etol**, the following are made by injection molding: instrument panel shield, steering wheel lining and other profile parts.

### Thermosetting plastics

Thermosetting plastics (reactive plastics) when reheated as a result of irreversible chemical reactions are transformed into hard, difficult-to-dissolve and non-softening (non-melting) substances. Therefore, the formation of parts from thermosetting plastics must precede the process of forming the plastic itself, because otherwise it will be complicated or impossible. Thermosetting plastics are obtained by polycondensation of low-temperature substances at an elevated temperature, which is accompanied by the separation of by-products (water, alcohol, etc.).

Thermosetting resin turns into a thermostable state at a temperature of 160...200°C. Among thermosetting resins, phenol-formaldehyde, polyester, epoxy, silicone (polysiloxane), melaminoformaldehyde, etc. are most often used as binders.

In the weakened state, most thermoset resins, compared to thermoplastic resins, change their physical and mechanical properties less when heated, have low cold fluidity, that is, creep under the influence of a constantly acting load.

Thermosetting plastics include phenoplasts, aminoplasts, press compositions based on organosilicon and polyester resins.

Phenoplasts are a long-known and common type of plastic mass. In its pure form, phenolaldehyde plastics (cast resin) are used very rarely due to increased fragility; they are reinforced with fillers, and also modified by combining with synthetic rubber and some thermoplastics. Phenoplasts are classified by filler.

In the production of automotive parts from phenolic plastics, so-called layered plastics are most often used: asbotextolite, textolite, carbolite.

Clutch and brake disc linings can be made *of asbotextolite with kaolin additive*.

Engine camshaft gears, engine water pump impeller support washers, camshaft support washers and other parts are made *from special textolite*.

The cap and rotor of the distributor breaker, insulators of the ignition coil and other parts are made *of carbolite*.

In the automotive industry, bodies and other large-sized and highly loaded parts are made from *fiberglass*.

On the basis of thermoplastic and thermoset resins, foams and foams with high elasticity are made. Foams, for example, polyurethane foam PU-101, are used for the manufacture of car cushions and backrests.

*Plastic masses are used during the repair of cars. Plastics in the form of pastes and powders are used to level the surface of the bodies.*

*Epoxy pastes* are used for leveling the surface of bodies. They have high adhesion to metals, significant mechanical strength, elasticity, low shrinkage, chemical resistance to petroleum products, water, solutions of salts, alkalis, acids, and some solvents.

*Epoxy resins* are also used as a structural, electrical insulating material and as a binder in the production of fiberglass and press compositions. They are used as cold and hot curing adhesives, and are also used for anti-corrosion and water-resistant coatings with good weather and light resistance, instead of welding when repairing bodies, cracks on the cooling jacket and in the valve box of the cylinder block, holes (up to 2 cooling jackets) of the cylinder block, cracks in the cylinder head, cracks in the cylinder head at the place of attachment of the sensor and water temperature indicator, holes up to 70 mm in the engine crankcase tray, etc. Repaired parts work reliably at a temperature not exceeding 100...120°C.

**Plastic powders** (PFN-12 and TPF-37) are used for leveling the surface of bodies and cabins by gas flame spraying at a temperature of 210...220°C. Coatings made of PFN-12 and TPF-37 powders are resistant to organic acids, oils, and have a high tensile strength.

**Polyamide (kapron) powders** are used to produce anti-friction layers of sliding bearings. Kapron, especially in combination with hardened steel, has exceptional wear resistance and practically eliminates the wear of the joint part, it has an insignificant coefficient of friction and therefore partially allows operation without lubrication. Kapron coating protects the metal from corrosion and the action of alkalis, weak acids, gasoline, acetone. It has low temperature resistance - the temperature in the friction node with kapron should be from -30°C to +80°C. Specific pressure and sliding speed are more strictly limited.

**Polyamide mass - kapron** is used in the repair of cars for the production of decorative and structural parts by injection molding. The nomenclature of products is wide, let's name the bushings of springs, the crosspiece of the cardan joint and the pivot of the rotary trunnion; speedometer drive gear, clutch release bearing oilers, drain taps, signal buttons, gear shift lever handles, etc.

### **14.3 CONTROL QUESTIONS**

1. What is the purpose of paint materials and what are the requirements for paint coatings?
2. What are the components of the paint coating?
3. What paint materials are used during repair painting?
4. How is the car body protected against corrosion?
5. What is the purpose of plastic materials used in automobile construction?
6. What materials are called plastics and what components are included in their composition?
7. How are plastics classified?
8. What plastics are most widely used in car construction?

## LECTURE 15. CONSTRUCTION AND REPAIR MATERIALS (part 2)

Lecture plan:

15.1 Adhesive materials.

15.2 Rubber, upholstery, sealing and insulating materials.

15.3 Control questions.

### 15.1 ADHESIVE MATERIALS

**Glues** are liquid or paste-like multi-component systems, the basis (binder) of which are high-molecular substances that have high adhesion to hard surfaces.

Gluing has long been used to connect wooden and rubber parts. In recent years, adhesives have been created that ensure a reliable connection of fabric materials, plastic parts and, finally, metal parts, as well as metal to non-metal.

As is known, adhesive and welded joints of parts abroad have long become an important component of the technology of manufacturing automobile equipment, as well as its repair. In particular, they are used for gluing windshields, some panels, etc.

Adhesive joints are not only very technological, but also provide high consumer qualities of automotive equipment. When gluing, the structure of parts or mechanisms is not weakened by holes for bolts and rivets and is not weighed down by the additional weight of fastening material and overlays. At the same time, the strength of the adhesive seam is often not inferior to the strength of mechanical joints.

Adhesive compounds are not without drawbacks. Many of them have low heat resistance, and some deteriorate over time due to the aging of the adhesive pro-layer.

The gluing process is generally reduced to the following operations: preparation of the surfaces to be glued, application of glue, pressing and hardening of the adhesive layer.

**The main indicator of glue quality** is the mechanical strength of the glue joint. The adhesive joint is tested for tearing and chipping, and the specific load at which the joint breaks is determined. The strength of the adhesive compound depends on the forces of adhesion and cohesion. In addition, liquid glue should spread well and wet the glued surfaces, and when it hardens, it should show minimal shrinkage. The strength of the hardened glue should be, if possible, not less than the strength of the material of the surfaces being glued together and should not decrease over time and with changes in temperature. The adhesive layer should not have a corrosive effect on the surfaces to be glued, interact with the products with which the glued product comes into contact during operation, and should not be destroyed under their influence.

**By purpose, glues are divided into universal and special.** Universal adhesives are designed for gluing heterogeneous hard and elastic materials in various combinations: metal-metal, metal-wood, metal-rubber, plastic-glass, etc. Special glues are used for gluing certain materials.

**The classification feature** of adhesives is the type of binder, according to which carbinol, phenolic, epoxy, and polyamide adhesives are distinguished. In addition, each type of glue in turn is divided into a number of brands. In this regard, the modern range of synthetic adhesives is extremely large.

The main type of universal adhesives are **synthetic adhesives** used in all branches of

technology. With the help of synthetic adhesives, it is possible to create high-strength, elastic, water-, oil-, and fire-resistant compounds that withstand vibration and dynamic loads. Synthetic glue in its most general form is a composition that includes: a binder (or their combination), a solvent, a filler, a hardener, and a hardening accelerator.

Thermoplastic and thermoreactive polymers (resins) are used as *a binder*. From thermoplastics, derivatives of acrylic and methacrylic acids, polyvinyl acetate, polyisobutylene, rubber, and rubber became the most common, and from thermosets, phenolformaldehyde, epoxy, and organosilicon compounds. Adhesives based on thermoplastic polymers form a reversible film that softens when heated.

To give a certain *viscosity*, acetone, alcohol, gasoline mixtures with ethyl acetate, butyl acetate with acetone or gasoline, as well as other solvents depending on the brand of glue, are introduced into the glue.

Powdered fillers (metals, glass, porcelain, cement, stone, etc.) are added to the glue to *reduce the shrinkage* of the glue during hardening and to prevent the appearance of cracks and the destruction of the adhesive film.

*A hardener and a hardening accelerator* are added to adhesives containing thermosetting polymers for the flow of processes associated with the formation of an adhesive film.

Adhesives based on epoxy resins have become widely used. These adhesives harden both at normal and elevated temperatures, have good physical and mechanical characteristics and high adhesion to metals and many non-metallic materials. They are characterized by good water, oil and gasoline resistance. When repairing, use EPO glues (TU 38-10972-82), EDP (TU 6-15-1070-82), epoxy putty (TU 6-15-662-85), etc.

Hot-curing epoxy glue UP-5-207 (TU 6-05-241-221-83) is used in the production of cars. The glue has a very good property of gluing oiled surfaces. It is used for connecting the inner and outer panels of the doors and gluing the flanges of the hood and trunk. Uncured glue is not washed off with cleaning solutions during the preparation of the body for painting. Hardening of the glue takes place in the dyeing chambers. In addition, butvaro glues are widely used - formaldehyde (BF) and carbonyl.

BF-2, BF-4 and BF-6 glues (butvaro-phenol-aldehyde) are widely used - alcohol solutions of thermoreactive phenol-formaldehyde resin modified (to increase the elasticity of seams) with butvar. The first two are used to connect solid materials, and the third (BF-6) is used to glue fabrics together and to attach them to metals, plastics, etc. All glues of the BF series are delivered to consumers in a finished form. The adhesive compound from them is dried at a temperature of 90-100°C for 1-3 hours.

When repairing cars, the glue is used for connecting friction linings with brake pads and is not suitable for gluing elastic and flexible materials, such as rubber, fabrics, etc.

Glue is also used during the repair of plastic parts. Thermosetting plastic parts are glued with resin adhesives (VIAM-B-3, BF-2, BF-4, K-17, etc.) based on epoxy phenol-formaldehyde and other resins. For gluing organic glass, dichloroethane or glue is used, which is a solution of organic glass sawdust in formic acid or dichloroethane.

Despite the well-known advantages of adhesive joints, they have not been widely used in the automotive industry, especially in the manufacture of car bodies. The main reason is the duration of the hardening process of the adhesive joints, which does not fit into the rhythm of the conveyor assembly. Cars roll off the assembly line in minutes, and

most of the most advanced adhesives harden within a few hours, and some within a day.

However, the situation has already begun to change: a new generation of adhesives have appeared that can polymerize in 3-30 seconds. The fact is that special additives are introduced into their composition - photoinitiators, which under normal conditions of a chemical reaction do not take place, but when irradiated with light of a certain wavelength, on the contrary, become powerful catalysts. Thus, all operations on applying glue and assembling nodes and aggregates can be performed in the same mode as when gluing without glue.

Before the start of irradiation, the glue remains in an uncured state. After that, the seams formed during assembly are exposed to ultraviolet radiation for a few seconds.

During this time, the photoinitiators split, turn into free radicals, which initiate an almost instantaneous chain reaction - the polymerization of the irradiated part of the glue.

But, unfortunately, the entire seam is polymerized only in the case of "transparent-to-transparent" surface connections. In the case of "transparent on non-transparent" - only its part exposed to radiation. Therefore, at present, ultraviolet curing glues are most often used for fastening automotive glazing (silicate glass is transparent in the range of 365-420 nm) and plastic products that are transparent in the range of 420 nm. The glues used are acrylic.

In addition to acrylic adhesives and sealants with auxiliary polymerization systems, the same anaerobic materials (which harden in the absence of contact with air oxygen) are increasingly being used. They are used for fixing, locking and sealing threaded and non-threaded connections.

For the automotive industry, as already mentioned, mastering adhesive technology is very important. It is no accident that many companies deal with it, in particular, glues (and adhesives in general) with ultraviolet curing.

The most famous of them is the Austrian Loctite. It produces more than a hundred brands of adhesives and sealants of various chemical natures, purposes (assembly of engines, transmissions, suspensions, steering, brakes and car bodies) and polymerization systems.

Loctite adhesives have a number of unique properties. In particular, they provide the adhesive seam with 99% optical transparency and an adjustable (1.4-1.55) refractive index value, which allows you to use them for gluing transparent materials and obtain an invisible adhesive seam. Some (for example, anaerobic Loctite 661) can work in the operating temperature range from -55 to 230°C, with a tensile strength of 35 MPa (350 kgf/cm<sup>2</sup>), at a break of 37-42 MPa (370-420 kgf/cm<sup>2</sup> cm<sup>2</sup>), with a setting time of 3 s. Therefore, this glue is used when installing bearings in housings and on shafts, for fixing rotors, gears, sprockets and pulleys on shafts, for attaching bushings, sleeves, cups to housings, sealing caps on engine blocks and gearbox housings. The use of such glue allows you to simplify the design (due to the elimination of keyways and pins) and, thanks to its instant partial hardening, to speed up the assembly process of assemblies and assemblies many times. In addition, when mounting bearings, for example, a layer of adhesive compensates for inaccuracies in the centering of assembly parts. Shafts and bearings mounted without misalignment, but with tension, last longer, they can be used repeatedly after disassembly and cleaning.

For the polymerization of Loctite adhesives (for their polymerization), you can use

ultraviolet lamps of the DRT-400 type and a specially designed installation that provides not only regulation of the intensity of the lamps' radiation, but also protection of the operator from ultraviolet radiation.

It should be noted that manufacturers often focus on foreign adhesive materials, while there are domestic ones that often surpass them in terms of performance and are much cheaper. Thus, one of the main enterprises - OJSC "Snizhynka" (former NITHIB) manufactures many adhesives for various purposes. Some of them are presented below.

Glue 88KR (TU 201-951-10-96). This is a modification in the series of chloroprene glues, which differs from its predecessors (88HII, 88CA) in increased strength, heat resistance, speed of setting, water resistance and stability of parameters during long-term use of adhesive joints.

The base of the glue is polychloroprene. It dissolves in such low-toxic solvents as gasoline, ethyl acetate, hexane. It is used for bonding rubber, rubber and metals (aluminum alloys and iron-based alloys), metals to each other, synthetic films, polyurethane, polyvinyl chloride, leather substitutes, leather, ABS plastics, laminated plastics, chipboard, wood, upholstery fabrics, etc. building That is, it is universal. It is vibration-resistant and fully maintains its performance in the temperature range from  $-30$  to  $+90^{\circ}\text{C}$ . The technology of its application is the simplest: seams are performed at room temperature and low contact pressure.

The most rational area of application of this glue is the connection and repair of interior decoration parts of truck cabins, passenger car and bus cabins.

"UR-Mono" glue (TU 201-951-1-96) is a universal polyurethane glue designed for joining leather, rubber, polyurethane, PVC, hard plastics such as ABS, metals, chipboard. It is colorless, transparent, single-pack, water-, vibration-, frost- and heat-resistant, low-toxicity. The peel strength of PVC skin exceeds  $50\text{ N/cm}$  ( $5\text{ kgf/cm}$ ). It works without the introduction of isocyanite hardeners, which simplifies the technology of its application.

Glue 75M (TU 201-28-72-96). It is made on the basis of thermoplastics (storage period - one to one and a half years). Along with such substrates as leather, rubber, polyurethane, wood and metal, it is able to glue polyethylene (rigid and film), polyamide, TEP and other polymer materials without preliminary chemical treatment. The strength characteristics of the seam are 1.5-2 times higher than the normative indicators. For example, the strength during delamination of compounds such as TEP-skin, skin-urethane exceeds  $50\text{ N/cm}$  ( $5\text{ kgf/cm}$ ). Capable of fast (10-15 min) gluing, water and heat resistant, low toxicity.

It is used in finishing and repair works. Recently, it has been used as an adhesive base when applying the so-called flock to textiles, plastics, and metal, which allows you to quickly obtain a velvety surface on these materials.

Glue "Ropid-5" (TU 201-196-90). Intended for gluing leather products, soft linings made of textile materials, rubber, synthetic leather. It consists of imported merchant-regulated chloroprene rubber "Skypren", reactive resins and metal oxides. It is a viscous (60-200 s according to VZ-246) white-yellow liquid.

"Krol" glue (TU 201-28-78-83) is a modified polystyrene glue for the production and repair of products made of impact-resistant and block polystyrene. Provides fast gluing of these materials within 15-20 minutes at room temperature and contact pressure, great durability of seams. It guarantees the absence of microcracks, which, as you know,

are inevitable when gluing polystyrene with active solvents. Vibration- and water-resistant, strong (adhesion strength to polystyrene substrates - up to 14.8 MPa, or 148 kgf/cm<sup>2</sup>), low toxicity. It is recommended to use when fixing and repairing parts made of polystyrene (radio units, receivers, instrument panel parts, etc.), as well as internal (facing) parts of refrigerator bodies.

ERK-1 adhesive pencil (TU 201-28-18-96) is a complex epoxy adhesive composition designed in the form of a solid rod, designed for express repair (wrapping) of microcracks and metal tears on pipelines and housings made of various metals and alloys (aluminum, copper, steel, cast iron). Oil-, gasoline-, vibration- and heat-resistant.

**Adhesives for rubber.** Glues for gluing rubber are divided into glues for gluing with vulcanization and for "cold" gluing. The industry produces rubber adhesives (for connecting rubber parts to each other) and special ones (for gluing rubber to metals, glass, plastics and other hard materials).

Of the special glues, two samples can be named: No. 61 and 88H. The first is prepared by dissolving rubber mixture No. 61 in "Kalosha" gasoline. Glue No. 88H is a solution in a mixture of ethyl acetate and gasoline of raw rubber No. 31-H, to which butylphenol-formaldehyde resin is added.

For gluing rubber parts to metal parts, glue No. 88, 88H, 61 or thermoprene is used. Gluing of rubber parts to wooden parts is done with the help of NC rubber glue.

Glue No. 200 (a solution of rubber mixture in gasoline) is used for gluing upholstery, rubber, cardboard and leather to metal.

Due to the toxicity of the components, they should be handled with care.

Modified rubber glue (TU 2385-004-05281725-97) (manufactured by JSC "Snizhynka"), which has a seam strength that is 2 times higher than the strength provided by traditional rubber glues, is suitable for gluing not only rubber, but also leather.

## **15.2 RUBBER, UPHOLSTERY, SEALING AND INSULATING MATERIALS**

### **Rubber**

Rubber is an expensive and, moreover, scarce material widely used in cars. These are pneumatic and massive tires, flexible hoses, shock absorbers, drive belts, sealing gaskets, sealing devices, couplings, conveyor belts, etc. Rubber is also widely used as electrical insulation in the manufacture of cables, wires, electrical machines and devices.

When repairing cars, special grades of raw rubber are used, the most important of which are interlayer tread and chamber rubber. All of them are intended for the repair of pneumatic tires by hot vulcanization.

A modern truck includes from 200 to 500 rubber parts, the production of which requires 250-400 kg of rubber, which is about 500-800 kg when translated into rubber. The cost of rubber products is from 10 to 40% of the total cost of the car.

**Natural rubber.** Rubber is a collapsible material that includes a number of components, the main ones being rubber, such as the characteristics that lie in the main power of gum.

Natural rubber (NR) comes from the so-called rubber plants - plants, mainly cultivated in the extremes of the tropical zone. Moreover, the best one is obtained from the sap (latex) of the rubber tree - the Brazilian Hevea. Wine is not produced in water, but not in naphtha products. On this ground the preparation of humic adhesives is started.

Chemically, natural rubber is a polymer of unsaturated isoprene in carbohydrates.

The high level of insaturation of the NA molecule allows it to reach a high level of chemical transformation. So, after the rupture of the valence bond between the third and quarter atoms of the carbon, sirka (vulcanization process), kisen (old gum), etc. can be added.

**Synthetic rubbers.** Born in 1932 For the first time in our region, synthetic rubber was synthesized, which became the main raw material for the ham industry.

Dozens of different types of synthetic rubbers (SR) are produced around the world.

During the production of automotive humic parts, the products of fusion polymerization of various monomers are widely contaminated. The most important representative of them, the copolymer of butadiene with styrene, is assigned the designation SKS (styrene). It should be added to the widest SCs (the part of the light generation of all SCs and PCs taken at once is 30%). The largest mass grade of SKS, which contains 30% styrene, is the SKS-30 brand. Gums on this basis want to compare with NK gums in terms of elasticity, heat and frost resistance, then surpass them in terms of wear resistance.

In addition, styrene rubber SKMS (methylstyrene butadiene rubber) is used. Pure rubbers are superior to natural ones for wear resistance, but sacrifice elasticity, warmth and frost resistance. When preparing car tires, isoprene (SKI-3) is used, which in its properties is close to natural rubber, and butadiene (SCR), which has high wear resistance. Chloroprenov (for example) and nitrile (SKN) rubbers have high oil and petrol resistance. These rubbers are used to produce parts that come into contact with naphtha products. Butyl rubber (a copolymer of isobutylene and isoprene) is vicorized for the production of inner tubes and the sealing ball of tubeless tires.

**Vulcanizing speech.** In pure appearance, natural and synthetic rubbers are used for drying (preparation of adhesives, sealants, medical plastic, gaskets). To increase the value of rubber, the process of vulcanization occurs - chemical bonding of rubber molecules with sulfur atoms.

As a result of vulcanization, for example, PC, which is most effective at a temperature of 140-150°C, produces vulcanized rubber (vulcanizate) with a resistance of approximately 25 MPa.

Before adding gum, add a little bit of sulfur in order to remove the vibration from the greater value and necessary elasticity. For example, gums that are used for the preparation of car tubes and tires contain 1-3% of the rubber content in them. Instead, the elasticity of the gum increases, but at the same time its elasticity changes.

**Quickly and again.** To speed up the vulcanization process, accelerators (thuram, captax etc.) are added to the rubber with vulcanizing resin, and to increase the efficiency of vulcanizers, active resuscitators (supplemented) Yuvachi). The most powerful agent is soot - powder-like carbon with particle sizes ranging from 0.003 to 0.25 microns. Soot, as well as other enhancers, is introduced into dry humic materials in significant doses - from 20 to 70% in relation to the rubber contained in them, increasing the value of humic materials by an order of magnitude.

In addition to the above-mentioned additives, in small quantities, you can add barnberries (for preparation), plasticizers (for easier molding), antioxidants (for enhanced processing processes), and polymerizers (for the preparation of porous or spongy parts of

gum) etc.

**Reinforcement of rubber products.** To increase the value of rubber parts, use reinforcement (fracture frames, metal braiding, etc.). The importance of humotissue germs is mainly determined by the importance of the reinforcement that is introduced into them. The elasticity of such particles, when stretched evenly from the humic acid, changes significantly, but it is preserved when compressed and the pressure is completely sufficient to prevent the parts from being damaged. The most important reinforced humic compounds that are used for automobiles include: humic fabric hoses, drive belts, etc.

Particularly suitable and expensive reinforced tires are car tires, for the production of which special fabrics are woven - cord, chafer, etc.

One of the main stages of the technological process when preparing gum is the equal mixing of all ingredients in the rubber, the number of which can reach up to 15. This process is completed in two gum mixers stages. The first stage - additional sums are prepared without any hassle or fuss; Another stage is the introduction of sirka and hasty care. The extracted hum mixtures are vicorized for the preparation of gum parts and for gumming tire cords, in order to strengthen the bond between the cord and gum and leak latexes and resins. The remaining operation after mixing all the ingredients is vulcanization, after which the humotechnical virus is added for curing. Syr gum (prosharkova, tread, tube) is cured during the repair of car tires and tubes using the method of hot vulcanization under a strong pressure, created by rubber seals.

Widespread use of gum is due to the fact that it is possible: up to and including large reverse deformations, which is one of the manifestations of highly elastic properties of the material (obviously, greater stretching when stretching for high-viscosity gums can be achieved gati 100%);

- low rigidity, equal to metal and wood, so that the building is strongly deformed under the influence of even small forces, which are thousands and tens of thousands of times less than the forces that cause the same deformations in metals;

- achieve a high value (for the shortest varieties of gum, the value when ripe reaches 40 MPa);

- low gas permeability and high water impermeability;

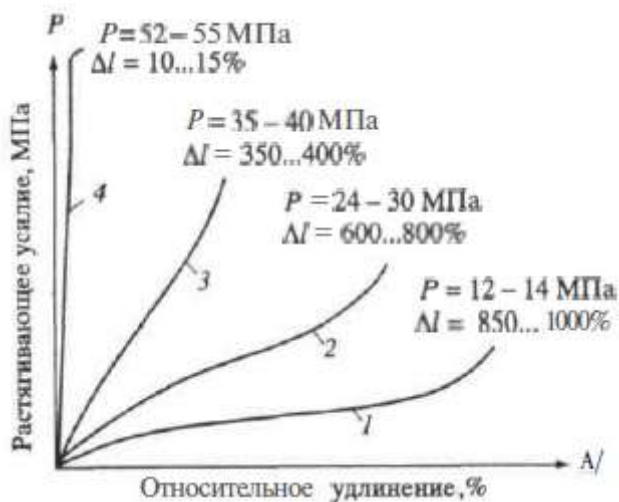
- high dielectric power.

**The values of the power** of humic material are characterized by the boundary of values, which is the tension that arises at the moment of rupture. To assess the intermediary values, it is necessary to use a special vantage machine if there is a tear of the humotechnical material of a strictly sized size. **Interface** – this is the number that is calculated when dividing the area, when the growth of the seed occurs, on the cob (before testing) cross-cut area, which is expressed in MPa.

**The mechanical power** of vulcanized gum is characterized by a number of indicators, the most important to observe when testing stretching and squeezing. The totality of the excess and excess water characterizes the elasticity of the humic material. The greater the difference between one and the other, the greater the elasticity of the material. The amount of elasticity is established depending on the particular part and is assessed by the values of the bearing and excess tension at expansion and the bearing pressure at the boundary tension, which are expressed in the range of up to the end of the expression.

The pulp of gum is characterized by a limit of its value – 15-20 MPa with a water pressure and expansion – 500-1000%. So, for example, gum, which is used for the production of inner tubes of automobile tires, ranges between 9-14 MPa, and usually increases by 550-600%.

With the movement of gum instead of sour, the elasticity of gum increases while its elasticity decreases. Figure 15.1 shows the change in the intermediary value P (MPa) and water pressure (%) for different types of gum.



1 - gum pulp without ingredients; 2 - gum pulp with ingredients; 3 - zhorstka gum;  
4 - hard gum (ebonite).

Figure 15.1 – Deposit of the inter-material (p) and liquid subtraction (A/) of gum during stretching

**Gumi hardness.** In technical minds, gum, like other materials, transfers a certain amount of hardness. To assess the greatest expansion of the filler using a TM-2 (Shora) hardness tester, the measure of hardness is the depth of the blunted edge at the shape of the cut cone of the head 1 (Fig. 15.2), expressed in the upper half of the scale.

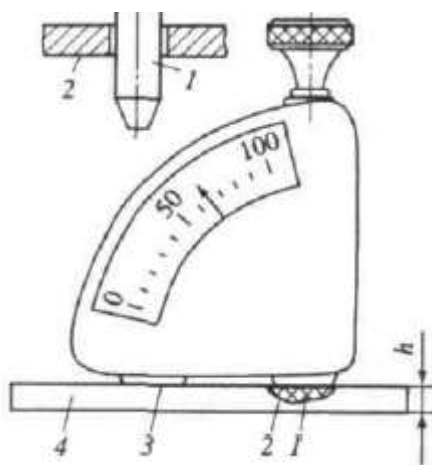


Figure 15.2 – Tverdomir TM-2 (Shora)

When the hardness of the TM-2 is set, it is necessary to press the gum with minimal

force, but sufficient for pads 2 and 3 to firmly adhere to the surface of the gum 4. thickness (h) not less than 6 mm. (The hardness for tire tread is between 55-65, and for rubber rubber, which is repaired during repair, -45.)

Extremely high hardness, which exceeds the permissible limits with full vulcanization of the correct choice of the grade of raw gum.

**Resistance to washing and coefficient of rubbing gum.** The indicator of wear resistance, known as the indicator of washing, is expressed by the expenditure of the sample tested, calculated in relation to one unit of work spent on washing.

For the help of this indicator, the resource of robots, low-tech chemical agents, and tire protection is indicated. The significant value for gum, cured prepared tires of passenger cars and vans, may be approximately 0.08 and 0.14 mm<sup>3</sup>/J.

With a change in temperature (Fig. 15.3), the power of the gum also changes greatly, and the performance of parts for various reasons changes both when heated (Fig. 15.4) and when cooled. The main unpleasant effect of a decrease in temperature is a change in the elasticity of the gum, which in a cooling world is approaching the point of collapse. Even at -45°C, the most compatible varieties of gum do not become deformed within the required boundaries.

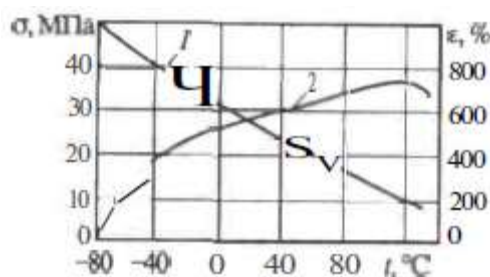


Figure 15.3 – Dependency between tension  $\sigma$  (curve 1) and bearing tension  $\varepsilon$  (curve 2) as a function of temperature  $t$  for rubber from natural rubber

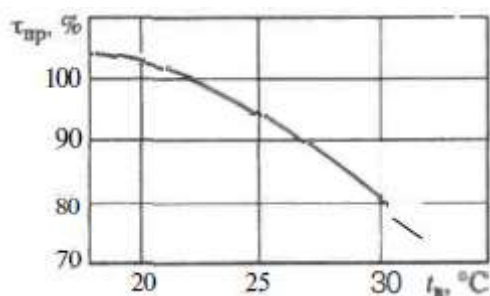


Figure 15.4 – Tire mileage  $\tau_{pr}$  depending on the temperature  $t_{\theta}$ .

Other gums, which are important in operational use, change with temperature changes only in an unfavorable way - softness, wear resistance and hardness change, and more and more In the future, the deformation will increase to the point of irreversible deformation.

Finding the reaction, yakslessly wounded at the Zberianniy Ta -Exy -Maimovikh Vobrovi, ε okslennya gumi, led to the serpent, fizichny of the mechanical power of the authorities.

The totality of all changes that occur in gum during the process of final oxidation are usually called *old*. The most unpleasant changes that come from age include an irreversible decrease in elasticity. Before important operational visits, it is necessary to eliminate humic germs from the influx of sedative exchanges, which are called the so-called light old age.

When there is a concentration of humic germs in the water, for three hours there is no noticeable influx of power from the humic. The greatest concern is for reinforced parts; metal reinforcement, which is consumed in the environment, is more susceptible to intense corrosion, and the fabric becomes less damaged and rots more quickly.

Upon constant contact with naphtha products, humic bacteria greatly increase in density, and their value, elasticity and hardness change significantly. In case of excessive contact of gum with gasoline, diesel fuel, lubricants, swelling, increased wear, decreased value, elasticity, and hardness may occur.

It is very important to properly preserve humic germs. Preservation of humotechnical germs should be carried out at moderate temperatures (+5...+25°C), as the temperature is increased, the cost of expansion decreases by 2-3 times.

In addition, it is necessary to preserve humotechnical materials with less stress and deformation. The butt can be tires that must be kept in a vertical position on racks with periodic changes (every 2-3 months) to keep the tread on the surface of the rack.

Re-installation of dismantled parts that affect the safety of the vehicle (tips, diaphragms) is not allowed.

### **Covering materials**

Covering materials are used for processing (upholstery) seats and car bodies. As a result, the interiors and cabins become more comfortable, their warmth and sound insulation improves. The type of materials used for the upholstery of cushions and seat backs, as well as the internal upholstery of the cabin and body, affects the appearance of the car, its quality, and the cost of maintaining the upholstery during use.

The main benefits of upholstery materials include: resistance to tearing and washing, beautiful decorative work, heat and sound insulation, durability, availability and low weariness.

Mechanical strength, elasticity and wear resistance are the most important benefits that depend on upholstery materials. There is a shortage of materials for upholstery of pillows and seat backs, and the stinking fragments are subject to mechanical pressure and aggregation. Regarding the value, elasticity and wear resistance of the upholstery, the terms of its service must be defined. In addition, upholstery materials can be easily cleaned from saws and other debris, and the upholstery of cushions and seat backs of passenger taxis and buses can be treated with disinfectant chemicals. At the same time, the upholstery materials must be treated well, without changing the appearance of the upholstery.

Upholstery materials that are vicorized for the manufacture and repair of cabins can contain the influx of naphtha products or their vapors. Therefore, the level of resistance of upholstery materials to the infusion of naphtha products also characterizes their softness. It is also important that the upholstery materials allow for repair, including by gluing.

As upholstery, various textile materials, hide substitutes, gum and other materials are used. The main place in body upholstery is occupied by textile fabrics. Before them are brought fabrics, fabric, cords, braid, fringe, etc. The power of textile materials depends on

the nature of the fibrous material and processing, as well as the structure and processing method of the finished materials. As upholstery materials, various fabrics are combined, including those with polymers applied to their surfaces, as well as synthetic melts.

Various complex materials such as upholstery material for car interiors have become increasingly used. For the face ball, different materials are used: fabrics, knitted fabrics, pieced khutro, pieced skin. Complex materials can be two-ball or three-ball. Two-ball complex materials consist of a front (main) ball and polyurethane foam. For three-ball complex materials, like a face ball, vikorist fabric and knitted fabric are used; Other balls are made of foam rubber and padded balls.

Complex materials are divided according to the tanning method, the method of applying the adhesive, and the type of glue. Duplicated materials are made up of different textile materials from different materials (Fig. 15.5). These materials are divided into laminated and bonded.



Figure 15.5 – Construction of duplicated materials

Laminated materials are made up of interconnected fabrics and polyurethane foam (Fig. 15.5, gr. 1-a, c) or fabrics with polyurethane foam and another fabric (Fig. 15.5, gr. 1-6, d, e).

Bonded materials are materials that are made up of two canvases connected to each other by turning one after another without foam rubber. As upholstery material for cars, complex upholstery materials are most often processed using adhesive or thermal (fire) methods.

When using the adhesive dubbing method, apply a thin ball of glue (polyisobutylene or polypropylene) to the inside of the main (face) ball of the material and then combine it with the lining material or foam rubber.

The fire method (the method of thermal melting of foam rubber) involves the fact that the surface of the foam rubber is melted in the half of a gas flame and is immediately duplicated with the material on one or two sides.

Nowadays, a large range of upholstered textile materials with enhanced hygienic characteristics and a varied range of styles have been developed - piled, voluminous, not only monochromatic, but more often - small parts. Widely woven caprovelor is a textile material that is folded into three balls; face - brushed warp knitted fabric (with polyamide thread), the other ball - polyurethane foam, lining ball of warp knitted fabric with

polyamide thread. The dubbing of balls is done using the flaming method. Surface thickness of the material - 420-480 g/m<sup>2</sup>. Upholstery of this type creates comfort in the car interior, since such material is characterized by breathability, volume, and a soft feel. The caprovelor is in short supply - it is old, low resistance to sealing, polyurethane polyurethane, etc.

As an upholstery material, complex textile material of the "hard" type is used the rest of the time. In this case, in the core of the face ball there is a fabric of finely patterned weave with textured polyester threads; like the crotch ball, the knitted fabric is made from polyamide threads. Fire tanning method. Surface thickness of material 430-530 g/m<sup>2</sup>. This material has satisfactory hygienic and operational properties. There is little evidence of speeches that are harmful for people using the fire tanning method; Possible destruction of polyurethane foam due to the influx of waste into an excessive middle ground, etc.

As an upholstery material, textile synthetic material - oxamite - is used. Oksamit has a garish modern appearance, volume, soft neck, good hygienic properties. The main shortcomings of oxamite, as an upholstery material, reduce the resistance of the pile to washing; replace the lint after an hour of use; straightening of the pile, which complicates the opening of the material; infusing the people with mischievous speeches, which are seen as a result of the fiery method of dubbing; the production value of polyurethane foam has been increased to renovation; the material is expensive.

The main tasks that designers, technologists and constructors face are to improve the quality of upholstery materials:

- Using environmentally friendly materials;
- Increased technological power in the processing of textile material for seat upholstery;
- Reduced quality of the material.

All these developments will be driven by the creation of new types of textile materials, driven by improved performance, environmental and technological advantages.

### **Sealing materials**

When assembling automobile components, there is a need to seal the places of contact of some parts with each other.

**Sealing materials** are used to seal the gaps between moving parts to prevent seepage and leakage of gas and liquid, as well as to protect the internal parts of units and mechanisms from dust, moisture and dirt. Seals for rotary and reciprocating motion are distinguished; in the first case, oil seals are used, and in the second - cuffs and oil seals.

These materials must have high strength, the necessary elasticity and at the same time a small stiffness, which ensures safety during installation and dismantling of products made of sealing materials and their tight fit even to very rough surfaces at relatively low pressures. In addition, some of these materials must be stable at high temperatures, in contact with oil products, water, etc. The materials used for the production of oil seals must additionally be wear-resistant. Most often, gaskets are made of paper, cardboard, parchment, fiber, cork, asbestos, felt, rubber.

**The most common lining materials include cork**, various types of chemically treated paper (parchment, cardboard, fiber, the maximum working temperature of which is 150°C), felt (heated no higher than 75°C), asbestos (workable up to 350°C), various brands of paronites (sheets made of rolled vulcanized mixtures of asbestos, rubber and

fillers, which allow heating up to 150°C), oil- and gasoline-resistant paronite MBP-5 (provides reliable sealing up to 250°C), ferronite 101 (reinforced 0 ), etc. Recently, new synthetic materials (for example, polyethylene foam PPE-2) have been used as gaskets in car bodies; non-woven materials from bast fibers (800JI, 920P, 1200JIP), etc.

Metals, rubber, plastics, fabrics, fibers, and felt are used in the production of oil seals both individually and in combination with each other.

***Metal materials*** are made from anti-friction alloys in the form of plates, foil or wire.

***Polymetallic materials*** are made of asbestos, jute or canvas as a soft medium, which is wrapped in foil or braided with wire.

***Rubberized materials*** are obtained from asbestos cloth or canvas impregnated with raw rubber and vulcanized. Fibrous materials are stuffing made of asbestos, jute, hemp, felt, etc., impregnated with binders. Felt seals are especially widely used.

### **Insulating materials**

Insulating materials include materials that practically do not conduct electric current. They are used as insulation in the production and repair of auto-tractor electrical equipment.

The following requirements are imposed on them: resistance to moisture, sufficient mechanical strength, high heat resistance (for some materials).

Mica, insulating paper, pressed foam, insulating tape, asbestos, ebonite, fiber, carbolite, textolite, bakelite and insulating varnishes are used as insulating materials.

***Mica*** is a refractory layered mineral that easily splits into thin transparent sheets. It is a dielectric that can withstand heating up to 500°C. Mica has high electrical insulating properties and is used as a dielectric in capacitors, collectors of electric generators and starters, in electric heating devices. Thin sheets of mica, glued together under hot pressing, are called micanite and are used as an insulating material between the collector plates of the generator, starter and other electric machines.

***Insulating tapes*** are strips of fabric coated on both sides with rubber glue, or polyvinyl chloride tapes coated on one side with an adhesive compound.

***Insulating paper*** is made from wood pulp treated with soda and sodium sulfate.

***Pressboard*** is produced in the form of sheets of hard cardboard. It is obtained from paper pulp impregnated with linseed oil. It is used for insulation in electrical machines.

***Insulating varnishes*** are a mixture of asphalt or bitumen, oil, organic solvent and sicativ. They are used to insulate the windings of pole coils of generators and starters, as well as to protect electrical parts from moisture and oil products.

## **15.3 CONTROL QUESTIONS**

1. What system is called glue?
2. How are glues divided?
3. Which adhesives are most widely used in the automotive industry?
4. What are the components of rubber?
5. What is the technology for obtaining rubber?
6. What are the main properties of rubber?
7. What materials are used for upholstering car interiors?
8. What materials are used as sealing materials?
9. What is used as insulation in the production and repair of electrical equipment?

## LECTURE 16. ENVIRONMENTAL PROPERTIES OF FUEL AND LUBRICANT MATERIALS

Lecture plan:

16.1 Toxicity of fuel and lubricants and other operating materials.

16.2 Impact of fuel and oil on the environment and people.

16.3 Environmental protection.

16.4 Control questions.

### 16.1 TOXICITY OF FUEL AND LUBRICANTS AND OTHER OPERATING MATERIALS

All types of fuels, lubricants and special liquids are poisonous (toxic) and flammable (flammable) to one degree or another. Fuels are also explosive. Therefore, it is necessary to know the main ecological properties of operational materials that are revealed when they come into contact with people and the environment. *The most important of these properties are toxicity, fire hazard, explosion hazard, and the ability to electrify.*

*Automobile gasoline*, as toxic materials, can enter the body through the respiratory system, skin and digestive tract. The concentration of gasoline vapors in the air should not exceed 0.3 m<sup>2</sup>/l. With short-term inhalation of air containing gasoline in the amount of 5...10 m<sup>2</sup>/l, acute poisoning occurs, the characteristic signs of which are headache, unpleasant sensations in the throat, cough, irritation of the mucous membrane of the nose and eyes, unsteadiness of gait, dizziness, excitement. When the victims are removed from the poisoned atmosphere, after some time, most of these phenomena disappear.

The concentration of gasoline vapors of 35...40 m<sup>2</sup>/l is dangerous for human health when inhaled for 5...10 minutes. At higher concentrations of gasoline vapors, rapid loss of consciousness and death may occur.

The greatest danger of acute poisoning by gasoline vapors is represented by work carried out in closed rooms when cleaning tanks and containers from gasoline residues in repair shops. With poor ventilation of such premises, the air quickly becomes saturated with gasoline vapors to dangerous concentrations, therefore, when carrying out the mentioned works, it is necessary to carefully observe the safety rules.

Serious poisoning can also occur when gasoline enters the body, when it is sucked in by mouth through a hose, or when parts of the fuel equipment are blown through the mouth. In these cases, severe pneumonia may develop.

*Leaded gasoline* contains tetraethyl lead (TES) as an antidetonator. Ethyl liquid, as well as pure TES, is a persistent poison that has a strong effect on the human body.

All operations with ethyl liquid, especially adding it to gasoline (ethylation), can cause poisoning, so they must be performed with careful observance of all preventive rules. In this regard, gasoline is ethylated only at plants with special mixing equipment. Ethylation or re-ethylation of gasoline without special equipment risks poisoning and is therefore strictly prohibited.

In leaded automobile gasoline, the amount of TES is very small, and the toxicity of such gasoline is many times less than the toxicity of ethyl liquid, but still they must be handled with care. If you observe precautions and the established rules for handling leaded gasoline, their use is as harmless as unleaded gasoline.

The experience of more than 60 years of using leaded automobile gasoline all over the world shows that by observing elementary precautions, it is possible to completely avoid the harmful effects of TPP on the human body. To prevent TPP poisoning, the following rules must be carefully followed when handling leaded automobile gasoline.

Leaded motor gasoline can only be used as fuel for engines. In no case should you use leaded gasoline for lighting lamps, extinguishers, forceps, blowtorches, lighters, petrol cutters, etc., for technical purposes as a solvent, washing parts, washing hands, and the like. There are known cases of poisoning when leaded gasoline is used outside of its intended purpose, for example, for cleaning clothes.

The poisonous effect of leaded gasoline is most pronounced when gasoline enters the body through the digestive tract. In this regard, sucking gasoline, as well as blowing gasoline lines and jets with the mouth to avoid accidental ingestion of leaded gasoline is strictly prohibited. For these purposes, you need to use special devices (pumps, etc.).

Under no circumstances should leaded gasoline be stored and transported together with food products. Meat, bread, flour, fats easily absorb TPP. Accidental spillage of gasoline can later lead to poisoning by contaminated food products. When contaminated products are boiled, their toxic properties do not disappear.

Containers made of leaded gasoline cannot be used for the transportation and storage of food products, as they will always contain a certain amount of TES.

Special attention in the prevention of leaded gasoline poisoning through the alimentary tract should be paid to the driver's personal hygiene. You can't eat food or put a cigarette in your mouth without first washing your hands with warm water and soap. It is possible to perform work related to leaded gasoline only in special clothing.

The danger of poisoning with leaded gasoline increases due to the ability of TES to accumulate on objects that surround us (walls and floors of buildings, clothes, concrete, plaster, wood and other porous materials, and so on). Degassers are used to decontaminate the soil, floor, equipment, containers and other objects in case they are contaminated with leaded gasoline.

Vapors of leaded automobile gasoline differ little in toxicity from unleaded gasoline. However, if a significant amount of leaded gasoline is spilled, there may be a danger of TPP poisoning, which is especially great in small unventilated garages of individual car owners. Under these conditions, the place where leaded gasoline was spilled must be degassed. If a large amount of leaded gasoline is spilled on a cement or asphalt floor, the spilled area should be thoroughly wiped with a dry cloth or ends and then washed with clean kerosene. After that, burn the rag or the ends.

Precautions must be taken when repairing an engine running on leaded gasoline. After the leaded gasoline has been thoroughly drained, all parts that came into contact with it and its combustion products must be washed with clean kerosene. These parts include: fuel pump, sump, fuel filters; carburetor, fuel lines, piston head, spark plugs, valves and valve seats, exhaust pipes, and so on. During minor engine repairs, all parts that will come into contact must be washed with a brush dipped in kerosene. With careful observance of all precautions, the handling of leaded gasoline does not pose any danger. The experience of using leaded gasoline confirms this. If leaded gasoline gets on the skin, it should be immediately removed with a rag soaked in kerosene, trying not to rub the liquid into the skin, and then wash the place with hot soapy water. If a significant part of the body is

covered with leaded gasoline, it is necessary to immediately remove the clothes, lightly wipe the affected part of the body with cotton wool soaked in kerosene, and then wash with soap, take a warm shower and put on clean underwear.

If leaded gasoline gets into the eyes, immediately wash the eyes with clean water. If leaded gasoline accidentally gets into the stomach, it is necessary to induce vomiting and wash the stomach with soda solution.

***The toxicity of diesel fuel vapors*** is usually higher than that of gasoline, but due to lower evaporation, the concentration of these vapors in the air is much lower. The maximum allowable concentration of diesel fuel vapors is 0.3 m<sup>2</sup>/l of air. Preventive measures and first aid are the same as when handling gasoline.

***The toxicity of exhaust gases***, especially when using leaded gasoline, is well known. Of the other components, carbon monoxide CO is the most dangerous, its MPC is 0.02 m<sup>2</sup>/l of air. Prevention of carbon monoxide poisoning consists in systematic monitoring of its content in the air at workplaces and car parking lots, in ensuring good ventilation. In order to prevent the inflow of exhaust gases, it is necessary to seal the pipelines of exhaust systems and reliable operation of ventilation.

***It is strictly forbidden to warm up in the car cabin if the engine is idling*** (that is, on a rich mixture), because exhaust gases gradually enter the cabin, creating a dangerous concentration. Since carbon monoxide poisoning occurs imperceptibly, this type of heating is often fatal. When providing first aid (before the doctor arrives), it is necessary to immediately take the victim to fresh air, cover with something warm and try to drink hot tea or coffee. If breathing has stopped, artificial respiration should be performed until signs of life appear.

***Lubricating oils (motor, transmission, industrial, etc.) and mineral-based hydraulic fluids are also toxic substances.*** Oils that contain additives should be treated with more caution than oils without additives, because the toxic substances for additives, which include sulfur, chlorine, phosphorus, zinc, lead and other elements, have not yet been sufficiently studied. In case of violation of the rules for handling oils and non-compliance with the rules of personal hygiene, they can cause eczema, follicular skin lesions, dermatitis, skin pigmentation and other diseases.

***Ethylene glycol*** and its aqueous solutions are antifreezes and are also very toxic. When ingested, they affect the central nervous system and kidneys. Glycol-based brake fluids have a similar toxic effect. The lethal dose of ethylene glycol is only 50 g (about 100 g of antifreeze). After working with antifreeze and brake fluids, hands should be washed with soap and water.

If ethylene glycol gets into the stomach, the victim should be given immediate assistance: thoroughly wash the stomach with water or a 2% solution of baking soda, artificially induce vomiting, cover, warm the victim and immediately call a doctor.

To prevent poisoning with cooling and brake fluids, it is necessary to strictly control their storage, transportation and use. There must be a clear inscription "Poison" on the container and in places where liquids are stored.

## 16.2 INFLUENCE OF FUEL AND OIL ON THE ENVIRONMENT AND HUMANS

The degree of influence of fuel and lubricant materials (FLM) and technical fluids on the environment is determined by three factors: chemical composition, operating temperature and the culture of handling them. Chemical composition is the dominant factor. It characterizes the potential ability of FLM to affect the external environment, and also determines the most ecologically and economically justified method of disposal of spent FLM.

*It is known that the main cause of air pollution is the incomplete and inefficient combustion of fuel.* Only 15...25% of it is spent on the operation of the machine, and the rest "flows into the pipe".

The exhaust gases of an internal combustion engine contain *more than 170 harmful components*, of which more than 160 are hydrocarbon derivatives, which are the result of incomplete combustion of fuel in the engine. The presence of harmful substances in exhaust gases depends on the type and conditions of fuel combustion. *The most harmful are carbon monoxide, hydrocarbons and nitrogen dioxide.*

The composition of exhaust gases depends on the type of fuel used, additives, engine operating modes, its technical condition, etc.

Combustion of fuels containing hydrocarbons with a high molecular weight leads to the emission of a large number of aromatic and other hydrocarbons. When organic fuels are burned, polycyclic aromatic hydrocarbons, some of which are carcinogenic, are found in their combustion products. These include benz(o)pyrene, 9,10-dimethylanthracene, benz(a)anthracene, dibenz(a,h)anthracene, etc.

According to the nature of the effect on the human body, two fundamentally different groups of hydrocarbons are distinguished: *irritant and carcinogenic*.

*Irritating hydrocarbons* affect the central nervous system and mucous membranes. They include aldehydes, all limiting and non-limiting compounds of carbon with hydrogen that do not belong to aromatic compounds. The greatest danger for humans is represented by hydrocarbon compounds of the carcinogenic group: 1, 2 - benzanthracene ( $C_{18}H_{12}$ ); 3, 4 - benzpyrene ( $C_{22}H_{14}$ ); 1, 2 - benzpyrene ( $C_{20}H_{12}$ ); 3, 4 - benzfluoranthene ( $C_{20}H_{14}$ ); 1, 2, 5, 6 - dibenzanthracene ( $C_{22}H_{14}$ ); coronene ( $C_{24}H_{12}$ ). Particularly dangerous is 3, 4-benzpyrene, which is also called benz(o)pyrene and which is a kind of indicator when other carcinogens are present in the mixture. Once in the human respiratory tract, polycyclic aromatic hydrocarbons gradually accumulate to critical concentrations and stimulate the formation of malignant tumors. The concentration of PAHs in the air has not been sufficiently studied. Obviously, they do not exceed 10–12...10–14 g/m<sup>3</sup>.

*The effect of carcinogenic substances* on a person depends on both the dose and the duration of their action. Neoplasms do not appear immediately, but only after a long time. It has been established that the human body intensively accumulates and retains benzo(o)pyrene in childhood and over 50 years of age.

CH hydrocarbons, especially of the olefin series, as well as CHO, participate in the formation of smog, which irritates the eyes, throat, and nose. Spills and flows of petroleum products are a significant factor in air, soil, and reservoir pollution. Pollution of water bodies causes tangible damage. Therefore, the composition and properties of water in the main sources of water use are standardized.

***The influence of oil products*** on reservoirs is manifested in the deterioration of the physical properties of water (turbidity, change in color, taste, smell); dissolution of toxic substances in water; the formation of a surface film of oil and sediment at the bottom of reservoirs, which reduce the oxygen content in the water. Oil and the products of its processing, falling into water, spread due to hydrophobicity on the surface, forming a thin oil film that moves at a speed approximately twice the speed of water flow. Upon contact with the shore and coastal vegetation, the oil film settles on them. In the process of spreading over the surface of the water, light fractions of oil partially evaporate and dissolve, and heavy fractions sink into the water column, settle to the bottom and form bottom pollution.

Table 16.1 shows data on the effect of petroleum products on the organoleptic properties of water and the body of animals.

The improvement of the equipment itself and the increase in the level of its technical readiness over the past 10...15 years have led to quantitative and qualitative changes in the composition of lubricants. In order to improve their functional properties, toxic individual components, which are characterized by certain toxicological properties, began to be added to the compositions. Such components (harmful substances) are functional additives that are added to lubricant bases in order to improve anti-wear, anti-seize (sovol, tricresyl phosphate), protective (benzo-tri-azole), antioxidant (paraoxydiphenylamine, phenyl-a-naphthylamine, ionol) effectiveness.

***Harmful substances include fuel and oil***, which, when in contact with the human body in case of violation of safety requirements, can cause poisoning, occupational diseases or deviations in health.

According to the degree of impact on the human body, all harmful substances are divided into four classes of danger: the first - extremely dangerous; the second - highly dangerous; third – moderately dangerous; the fourth - low risk.

Table 16.1 – Limit concentrations of petroleum products in water for different water uses

Речовина	Граничні концентрації (мг/л), що впливають на:			ГПК у воді водоймищ, мг/л	
	органолептичні властивості води	санітарний режим водоймищ	організм тварин	господарсько-питного і культурно-побутового водовикористання	рибогосподарського водовикористання
1	2	3	4	5	6
Нафта багато-сірчиста	0,1	3	300	0,1	0,05 нафта і нафтопродукти в розчиненому і емульгованому стані
Нафта інша	0,3	3		0,3*	
Мазут	0,3	3		0,3*	
Бензин	0,1	–		0,1*	
Гас	0,1	–		0,1*	
Бензол	5,0	25	0,5	0,5**	0,5**
Толуол	0,5	25	200	0,5*	0,5*
Ксилол	0,05	1	0,1	0,05*	0,05*
Стирол	0,14	10	1000	0,1*	0,1*
Нафтонові кислоти	0,3	100	200	0,3*	–
Етилен	0,5	10	1,5	0,5*	–
Пропилен	0,5	10	1,5	0,5	–
Тетраетил свинець				відсутність	

Note.

\*Normalized according to organoleptic signs of harmful effects.

\*\*Normalized according to sanitary and toxicological signs of harmful effects.

The hazard class of harmful substances established by this standard depending on norms and indicators is given in table 16.2.

Table 16.2 - Hazard classification of harmful substances

Indicator	Norm for the hazard class			
	1	2	3	4
Maximum permissible concentration of harmful substances in the air of the working area, mg/m <sup>3</sup>	<0,1	0,1...1,0	1,1...10,0	>10,0
The average lethal dose when administered into the stomach, mg/kg	<15	15...150	151...5000	>5000
The average lethal dose when hitting the skin, mg/kg	<100	100-500	501...2500	>2500
Average lethal concentration in air, mg/m <sup>3</sup>	<500	500...5000	5001...50000	>50000
The coefficient of possible inhalation poisoning	>300	300...30	29...3	<3
Zone of acute action	<6,0	6,0...18,0	18,1...54,0	>54,1
Zone of chronic action	>10,0	10,0...5,0	4,9...2,5	<2,5

*Mineral oils* are a real threat to human health in those cases when they contain light hydrocarbons (gasoline, benzene), or when the formation of oil mist or oil vapors (when heated and sprayed) is possible.

Human respiratory tract and lungs are more sensitive than other organs to the influence of oil vapor and oil mist. Inhalation of oil mist with suspended particles from 1 to 100 microns causes poisoning. Among patients with lung and bronchial cancer, many people were found who were long-term exposed to vapors or mists of mineral oils and their emulsions. The danger of poisoning by oil vapors or mists increases dramatically if the oil contains sulfur compounds.

In the presence of sulfur in the oil, conditions may arise for the formation of hydrogen sulfide (H<sub>2</sub>S), which causes poisoning with a sudden loss of consciousness. The toxicity of oils also manifests itself with frequent exposure of oils to open areas of the body, with long-term work in oil-soaked clothes. Systematic contact with oil can cause an acute or chronic disease of the skin of the body. The most frequent follicular lesions of the skin, which are diseases of hair follicles and sebaceous glands. These diseases are known by the name of oil or kerosene eels, and are observed in mechanics, turners, tractor drivers, drivers, storekeepers and other workers who deal with oils on a daily basis.

There are known cases of damage to the skin (mostly the hands) by oils that hit the skin under great pressure. This is observed when spraying oils under pressure with special pumps during tests of diesel engines and oil pipelines. At the same time, the oil penetrates the skin and penetrates into the subcutaneous tissue, causing the development of swelling with pain and numbness of the affected areas. In case of contact with infected areas, abscesses and areas of skin necrosis may form. Oils can cause eczema, dermatitis, skin pigmentation and even a more serious disease - the formation of warty growths that turn into cancer. The toxic properties of oils increase with an increase in their boiling point,

acidity, as well as with an increase in the content of aromatic hydrocarbons, resins and sulfur compounds in their composition.

Oil vapors mixed with air are explosive in the presence of a spark or other open source of fire.

For all mineral oils, the real danger of the formation of explosive concentrations of oil vapor occurs when the oils are heated in a closed container to a temperature above 100°C. But it should be borne in mind that if a small amount of fuel is found in the oil, then when such oil is heated, an explosive concentration can be formed even at a temperature below 100°C.

Ignorance of properties, unqualified handling of oils and failure to take precautions when working with them can lead to serious, sometimes irreparable consequences. But no matter how great the toxicity, fire and explosiveness of oil products and their health hazards are, the likelihood of a fire or explosion will be minimized if you follow the rules of personal hygiene and prevent the occurrence of fires and explosions, as well as skillfully use fire extinguishing agents and provide first aid to victims.

The specifics of working with petroleum products impose special requirements for safety techniques when working with them. The toxicity, explosiveness and easy flammability of petroleum products require strict compliance with the rules of personal and fire safety, as well as recommendations, from all workers related to transportation, storage, quality control, use of fuels and lubricants, refueling of equipment, maintenance of machines and their repair on reducing the level of pollution of the surrounding atmosphere, soil and reservoirs with oil products.

### **16.3 PROTECTION OF THE ENVIRONMENT**

***Atmospheric pollution*** with vapors of oil products affects the environment and human health. Vapors of petroleum products belong to the IV group of harmfulness. They can cause heatstroke, because in windless weather it is above the soil surface, especially when oil storage facilities are located in low-lying areas. In addition, the mixture of hydrocarbons with nitrogen oxide in the air contributes to the petrochemical formation of such harmful compounds as ozone, peroxyacetyl, nitrates, aldehydes, aerosols. These substances irritate the mucous membrane of the eyes, damage vegetation, some of them are carcinogenic.

***Reducing hydrocarbon vapors is the most effective way to fight petrochemical pollution of the atmosphere.***

The maximum allowable one-time concentration of gasoline vapors for the atmospheric air of populated areas is 5 mg/m<sup>3</sup>, the maximum allowable concentration for the "working zone" is 100 mg/m<sup>3</sup>.

***Contamination of soil and groundwater*** is caused by leakage of petroleum products. The main feature of leaks is that they are uneven in area and time. For example, leakage of petroleum products at a rate of two drops per second leads to their loss of 130 l/month. Outflow in the form of drops that turn into a thin jet reaches 200 l/month, and outflow in the form of a jet with a thickness of 2.5 mm leads to losses of up to 2.5 thousand l/month.

The territories are polluted, mainly due to contamination of underground water and soil. Petroleum products that reach the surface are filtered vertically through the thickness

of the soil aeration zone and reach the groundwater level, where they accumulate and spread over the aquifer.

Soil and underground water pollution is distributed unevenly over the entire area, in the form of individual spots located in places where petroleum products leak. Therefore, when the issue of carrying out remediation works is decided, these works should be carried out not on the entire territory, but on individual local areas of maximum pollution.

Local treatment facilities (sand traps, oil catchers, neutralization stations, flotation installations, etc.) should be used at oil depots, the construction of which will allow to exclude discharge of pollutants into wastewater.

Local sewage treatment facilities must provide surface wastewater treatment in case of oil spills, emergency situations, and general pollution of the oil storage area.

***The main indicator of the operation of sewage treatment plants is the quality of cleaning.***

***Wastewater before discharge*** into the reservoir must be cleaned in accordance with the existing regulatory requirements for the concentration of oil products in them - 0.05 mg/l. The concentration of suspended substances should not exceed 10.5 mg/l.

As a result of the production activity of the motor vehicle complex, there is active pollution of the atmosphere, hydrosphere, and lithosphere with active toxic substances. ***Motor transport is one of the main sources of air pollution.*** Automobile transport refers to moving sources of pollution, widely found in residential areas and places of recreation. Toxic emissions of internal combustion engines are spent and crankcase gases, fuel vapors. The main share of toxic impurities enters the atmosphere with the exhaust gases of internal combustion engines. With crankcase gases and fuel vapors, about 45% of hydrocarbons enter the atmosphere from their normal emission.

Regardless of whether the gasoline engine is running or not, gasoline vapor passes through the fuel system. When the engine is running, from 4 to 12% of  $C_nH_m$  emission occurs due to fumes. Daily hydrocarbon vapors from the carburetor and fuel tank of a car amount to about 40 g, and from the tank of trucks - up to 150 g. It is estimated that in a hot climate, each car loses 60...80 liters of gasoline during the year due to evaporation. In addition to hydrocarbons coming from the fuel system of cars, a significant amount of them enters the atmosphere when refueling vehicles. At the same time, fuel losses can reach up to 1.5 g per 1 liter of refueled fuel.

Diesel fuel must also meet certain environmental indicators regulated by DSTU 7688:2015. At the same time, according to the requirements of Euro 5, the mass fraction of sulfur is allowed no more than 10 mg/kg, the concentration of actual resins is no more than 30 mg/100 cm<sup>3</sup>, and the ash content is no more than 0.01%. The toxicity of diesel fuel vapors is usually higher than that of gasoline, but due to lower volatility and good tightness of the diesel fuel system, the concentration of vapors in the air is much lower. The maximum allowable concentration of diesel fuel vapors is 0.3 m<sup>2</sup>/l of air.

For clarity of the above, the scheme of formation of harmful emissions is presented in Figure 16.1.

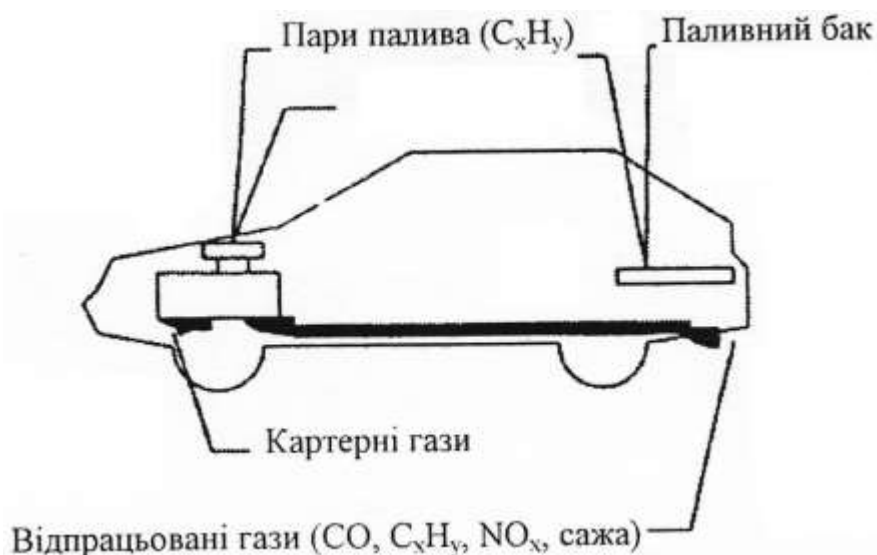


Figure 16.1 – Sources of harmful toxic emissions in a car

As for the effect of automobile transport refers on the lithosphere, it should be noted that soil pollution by road transport as a result of the waste of its work is fuel and lubricants, tons of discarded tires, spent batteries, damaged car parts and scrapped cars and bodies themselves. As a result, large areas of fertile soil are not used.

But the most dangerous impact is the pollution of the hydrosphere by the auto-tractor complex. Numerous acids, alkalis, oils enter the reservoirs through groundwater, from which the population's water supply originates.

On average, road transport discharges about 62,000 tons of suspended solids and more than 2,100 tons of petroleum products into wastewater annually. The problem of disposal of oil waste and precipitation from treatment facilities is acute.

Currently, there are various methods of cleaning wastewater discharged by motor vehicle enterprises. For example, chemical cleaning uses appropriate chemical reagents or additives that remove or neutralize harmful chemical impurities in wastewater. Closed systems are used, where synthetic detergents, after being used for their intended purpose (washing vehicles, units, assemblies, parts, etc.), are not discharged into the sewer system, but are regenerated and reused. In such systems, the spent washing solution settles, then the slag that fell to the bottom of the tank and oil products that floated to the surface are removed from it. If the solution is heavily contaminated with fine particles, it is subjected to a second cleaning cycle using coagulants. As such reagents, in particular, iron sulfate and magnesium hydrate or their mixtures are used. Saturation of water with oxygen (ozone) and chlorine in order to destroy dangerous microbes can be attributed to this category of purification. Ionization (activation) of oxygen and its injection into the purified water are accompanied by rapid oxidation of many harmful impurities and their precipitation in the form of flakes, which are then removed from the water. The presence of active oxygen has a detrimental effect on bacteria, fungi, and viruses.

The main direction of saving water for industrial needs and preventing pollution of the hydrosphere is the creation of closed circulating water supply systems at enterprises, which, as a rule, is cheaper than large water treatment facilities. In closed systems, a certain amount of water, having performed a given function (for example, cooling units), is restored

to its original quality, that is, it is cooled, cleaned of pollutants and reused for its intended purpose (Fig. 16.2).

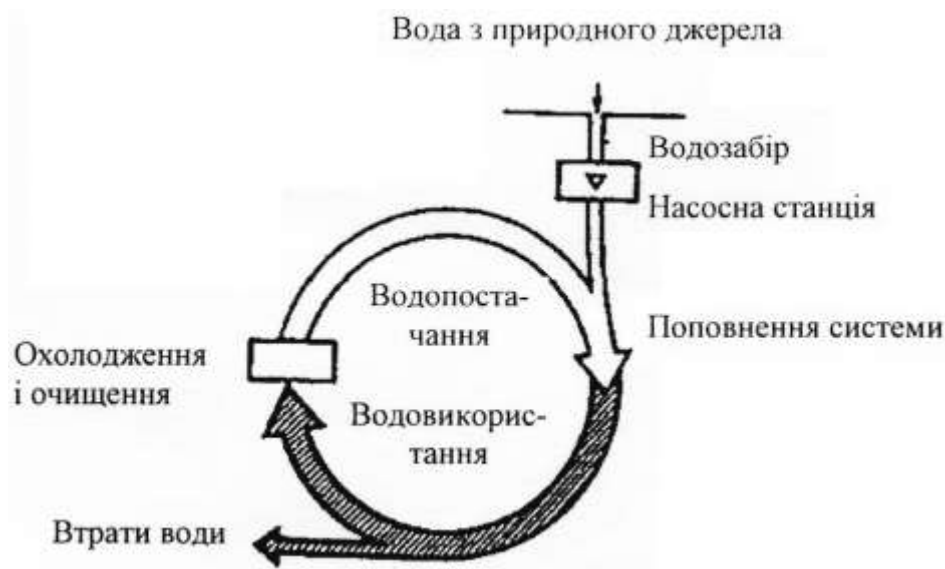


Figure 16.2 – Schematic diagram of circulating water supply

The problem of environmental pollution has become particularly acute in the modern period of the scientific and technical revolution, which is characterized by high rates of growth of production forces. One of the most widespread sources of environmental pollution are motor vehicles and work equipment, as well as enterprises for their maintenance.

Stationary and mobile means of delivery, storage and distribution of petroleum products and liquefied gases have also become sources of pollution of water and air basins. The negative impact of these means on the environment is manifested to a greater extent in large cities with a high density of buildings and a significant concentration of motor vehicles, and the potential danger of this impact is increasing. The specific weight of gas stations in the total emission of atmospheric air pollution in the largest cities of some countries reaches 10%. For example, according to the Tokyo Bureau of Pollution Control, more than 7% of hydrocarbons emitted into the city's atmosphere are accounted for by PZP. According to US data, more than 2,000 tons of hydrocarbons are released into the environment at the Los Angeles landfill.

Considerable attention is paid in our country and abroad to issues of the influence of gas stations and road transport on the environment and the development of methods of its protection. The main sources of environmental pollution during the operation of stationary and mobile fueling equipment are emissions of toxic substances into the surrounding space.

Factors affecting the degree of environmental pollution are very diverse and often interdependent. According to the nature of action, sources of pollution can be divided into two groups - *permanent and accidental*.

*The first group includes:* pushing out vapors of petroleum products and liquefied gases from tanks when they are filled ("big breaths"); pushing out vapors of petroleum products and liquefied gases from the fuel tanks of cars when they are refueled ("small

breaths"); displacements arising as a result of daily temperature changes in the gas space of tanks; extrusion during ventilation of tanks due to their insufficient tightness; with car exhaust gases.

***The second group includes:*** leaks of petroleum products when tanker trucks and refueling stations, fuel tanks of cars are overflowing, and when petroleum products are drained into storage tanks, oil depots, and consumer warehouses; leaks during maintenance and repair of technological equipment, stationary and mobile equipment; emergency leaks, etc. Atmospheric air pollution during the operation of stationary and mobile fueling facilities in combination with the concentration of a significant number of motor vehicles on the territory of the PZP determines two main types of harmful substances: hydrocarbons (gasoline vapors) and gases from used cars, the main component of which is carbon monoxide.

Studies of the temperature regime of the gas space of underground tanks at some stationary PZP showed that the amplitude of daily temperature fluctuations in them is very small. In addition, the turnover ratio of PZP tanks is very high, the interval between their filling does not exceed 2 days. Therefore, emissions of hydrocarbons into the atmosphere from "small breaths" are practically absent. At the same time, it was noticed that for technically sound tanks, with their correct operation, emissions from ventilation occur only when the probe pipe is opened to measure the level of petroleum products. Therefore, the main sources of

pollution of the atmospheric air of PZP is "big breaths" and emissions of vapors from the fuel tanks of cars when refueling. The amount of vapor-air mixture emitted during "big breaths" depends on the physico-chemical properties of the oil product, the temperature regime of the tanks, the degree of their filling, the depth of the deposit, the type of respiratory equipment and other factors.

***Emissions from the fuel tanks*** of cars and tractors during refueling occur as a result of the vapor-air mixture saturated with hydrocarbons being pushed into the atmosphere. Exhaust gases from cars and tractors contain a large number of different chemical compounds, among which hydrocarbons and carbon monoxide are of special interest from a hygienic point of view. The qualitative and quantitative composition of exhaust gases depends on a number of factors: the type of engine, its design and technical condition, power, mode of operation, type of fuel used. There is a significant difference in the content of toxic components in the exhaust gases of carburetor and diesel engines. During comparative tests of machines with the same technical characteristics, running on gasoline and liquefied (compressed) gas, significant advantages of the latter in relation to the content of toxic substances in exhaust gases were established. The mode of operation of the engine has a very significant effect on the content of carbon monoxide and hydrocarbons in exhaust gases.

Sources of contamination of soil and water bodies near PZP are mainly leaks of petroleum products (sources of the second group). Leaks of petroleum products during refueling occur as a result of overflowing fuel tanks of cars and account for about 50% of all leaks spilling on the fuel tank of petroleum products. Their volume depends on the qualification and discipline of the PZP staff and drivers, as well as on a number of technical and technological parameters, and the latter are subject to certain dependencies. Leaks of oil products when poured into the reservoirs of the PZP concentrate, as a rule, in

the drain wells, destroy them and penetrate into the soil. The amount of spilled oil products depends on the frequency and speed of draining, the tightness and reliability of the draining equipment and the qualifications of the personnel.

Leaks of oil products in the event of equipment malfunction, its maintenance and repair occupy a significant place in the general picture of pollution of the environment. Leaks from hydraulic systems of refueling equipment most often occur as a result of wear of sealing parts. During maintenance and repair of the equipment, leaks are also inevitable due to the imperfection of the design of individual nodes. Leaks of petroleum products are a particular danger when the hermeticity of the PZP tanks is broken due to corrosion. The size of these leaks can be very large. This is explained primarily by the fact that they do not appear immediately and it is extremely difficult to prevent their occurrence, because the existing design of horizontal tanks and their installation technology practically do not allow periodic inspections and control of the degree of corrosion of their walls and bottom.

A number of technological, organizational and technical measures have been developed in order to reduce the pollution of the ambient air of the PZP by emissions of toxic substances in our country and abroad.

One of the main measures to reduce the pollution of the atmospheric air by vapors of petroleum products of PZP is to return the vapor-air mixture emitted during "big breaths" to the tank of a tanker truck or fuel tank. The principle of operation of the ring system is very simple. The neck of the tank truck is connected to the ventilation pipeline of the fuel tank by means of a hose and a special shut-off valve. The vapor-air mixture displaced from the tanks during the draining of petroleum products is returned to the tank truck, which is being emptied. At the oil depot, when the tanker truck is filled with petroleum products, this vapor-air mixture is forced into the condensers for its recovery from gasoline. Such a system allows you to recover 80...90% of gasoline contained in containers that are thrown away during "big breaths". In addition, when sealing the gas space of PZP tanks and car tanks, the time for draining oil products is reduced by 18...20%. Despite its high efficiency, this system did not spread in Ukraine. This is explained by the fact that there is a need to equip the entire fleet of tank trucks, tanks and gas stations with special devices, and this is connected with the increase in the number of operations when draining petroleum products.

Another effective way to reduce the emission of toxic substances into the atmosphere is the use of gas lining of PZP tanks. For this, the gas spaces of groups of tanks occupied by gasoline are connected by pipelines into a single gas equalization system that communicates with the atmosphere through a breathing valve.

However, it is practically impossible to achieve effective operation of the gas equalization system, which includes the SMDK-50 breathing valve, which is currently widely used in the PZP, and is designed for an excess pressure of 0.002 MPa. The use of a high-pressure breathing valve in the gas equalization system, which is designed for an excess pressure of 0.015 MPa, gives good results. Such a system allows you to avoid emissions from "big breaths" in most cases.

Extremely important *is the problem of reducing the toxicity and amount of car exhaust gases*. Efforts are being made to solve it in our country and abroad, extensive research is being conducted on the creation of special fuel additives and the use of various types of neutralizers. However, to date, the main measure to reduce environmental

pollution with exhaust gases remains the maintenance of cars in a technically sound condition and regulation of their fuel supply system.

Reducing the concentration of toxic components in exhaust gases can be achieved by keeping cars in a technically sound condition, adjusting their fuel supply systems, installing a catalytic converter in the exhaust system, and injecting water into the engine. The most effective measure to reduce environmental pollution is to use a combination of the last two methods. Such a combined exhaust gas cleaning system has been tested on quarry dump trucks. The system includes two catalytic and one liquid neutralizers.

As already noted, the amount and toxicity of exhaust gases depend on the time and mode of operation of the engine. Based on this, in the conditions of the PZP, the main factor in reducing atmospheric air pollution by exhaust gases is the reduction of the time spent by motor vehicles on the territory of the PZP. This can be achieved by intensifying the refueling process, reducing downtime and reducing the need for maneuvering on the station territory. The most effective way to solve these problems is to choose a rational planning scheme of the PZP. Due to the selection of the optimal planning scheme of the GOP, the possibility of simultaneous use of all fueling means is ensured, the distance from the fueling places to the station building is reduced, and the number of necessary maneuvers to approach the gas station is reduced. All this makes it possible to significantly intensify the refueling process, increase the throughput capacity of gas stations and, ultimately, reduce environmental pollution by car exhaust gases.

Reducing the harmful effects of emissions of toxic substances on the PZP is facilitated by green plantings, their effectiveness largely depends on the type and method of their planting.

#### **16.4 CONTROL QUESTIONS**

1. Name the main ecological properties of operating materials.
2. What effect do gasoline vapors have on the human body?
3. Tell about the toxicity of diesel fuel vapors.
4. Are car exhaust gases poisonous?
5. What other operating materials are toxic substances?
6. List the most harmful substances in exhaust gases.
7. Name the main environmental pollutants.