

Production of mineral oils and regeneration of waste motor oil

The head of scientists teams

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Project Summary:

The method of obtaining conditioned base oils from the Georgian and Azerbaidzhan oils is considered in the presented project. Petroleum oils will be applied as the substitute of sharply deficient and expensive silicone liquid, basic component (58-60%) of lubricants at the formation of synthetic and artificial and complex fibrous threads sintoks-12 and sintoks-20 M

According to our preliminary data the color indices and viscosity of base oils will be on the level of best foreign samples.

Petroleum oils, obtained by us, can be applied as non-blocking agent in the aerosol containers (where it will replace silicone liquid), utilized in the molds during the extrusion of technical plastic parts. It is especially important that the application of petroleum oils in the aerosol container during the extrusion of different technical parts, in contrast to silicone liquid, does not leave on the surface of parts the thin layer of film. Film on the surface of parts hampers normal electrical conductivity.

In the project it is examined also the regeneration of the mixtures of waste motor oils of internal combustion in gasoline and diesel engines to the level of fresh for their repetitive use. Regenerated oils are subject to compounding by the additives of functional

designation. Regenerated compounded motor oils will have low coefficient of friction, high antiwear properties and prolonged period of service.

Taking into account preliminary data of regenerated oils we think that they will be at the same level with foreign contemporary motor oils;

The represented problems of the project are extremely urgent and practical. Their positive solution will give significant economic and ecologic effects.

Project Description:

1.11 Introduction

What's the problem?

Obtaining the valuable petroleum products, which correspond to the contemporary requirements according to the operational, economic and ecological characteristics, is one of the urgent problems of deep petroleum refining.

The increased requirements for reliability and effectiveness of the work of technics led to the significant hardening of operating characteristics of petroleum products. Legislative reports for the protection of environment require obtaining petroleum products with improved ecological properties. In connection with this in the recent years the quality of petroleum mineral oils is considerably increased, thanks to the wide utilization of hydro-catalytic processes and contemporary additives, which raise operational and ecological characteristics. [1, 2, 3, 8, 31, 37]

In the recent years there are noticeable shifts in the improvement of the quality of base oils, which made it possible to produce new types of oils and to spread the productions of a number of high-index motor oils; however, the share of these oils in the total volume of production must be increased. For an increase in production and improvement in the quality of base oils it is necessary together with new facilities to concentrate efforts of researchers, designers and industrial enterprises for modernization and further perfection of technology of the production of oils. The modernization of technology must be directed both toward the improvement in construction of extraction equipment and toward the perfection of technology of separate processes and the scheme of production of oils as a whole.

There are created the new schemes of production of oils (B.V. Gryaznov, N.N. Kachlishvili, I.Ya. Edel'shteyn, V.Z. Zlotnikov, I.Ya. L'vov).

In the work of B.V. Gryaznov it is given the development of the scheme of treatment for raw material by "single flow" with utilization of a process of preliminary hydro-improvement; in this case the processes are combined into one solid technological block, which makes it possible to considerably increase oil outlet and to obtain oils with ?? 100 and above.

1.12 Literature Search

What are other people doing?

According to published data petroleum oils represent the mixture of high-molecular paraffin, naphthenic and, in particular, aromatic hydrocarbons with small admixture of tar-asphaltene substances. [3, 4, 5, 6, 35]

In accordance with the fields of application oils can be divided into lubricating and special purposes. The lubricating oils, used practically in all areas of technology, depending on designation fulfill the following functions: decrease the coefficient of friction between the

friction surfaces, reduce the intensity of wear, protect metals from corrosion, cool rubbing parts, remove wear products.

The special oils serve as working fluids in hydraulic gears, electrical insulating medium in transformers, capacitors, cables, oil breakers; they are used during the preparation of grease, additives; as the basic component in the lubricants for formation of artificial and synthetic fibrous threads, and also as non-blocking agent for molds during the extrusion of parts made of plastics. [5, 6, 7, 29]

Usually commercial (motor) oils are being obtained by addition the compositions of additives to base oils. Additives are substances, which amplify the positive properties of base oils or imparting to them necessary new properties. [4, 5, 9, 32] There are distinguished three types of base oils:

Mineral, obtained by the synthesis of organic matters;

Synthetic, obtained by the synthesis of organic acids;

Partially synthetic, consisting of the mixture of mineral and synthetic oils.

By the method of liberation mineral base oils are subdivided into:

Distillate, obtained from the oil fractions, liberated with the vacuum distillation of mazut with the limits of temperatures of boiling 350-500oC. For obtaining high quality oils there are separated four-five narrow oil fractions at the temperatures of boiling 20-60 oC;

Residual, obtained from the deasphalting agent, liberated at deasphalting of goudron with liquid propane; residual oils can be obtained also during the treatment of fraction at 500-560 oC, liberated during the deep vacuum distillation of mazut;

Compounded (mixed), obtained by mixing in the specific proportions of distillate and residual base oils.

Oil distillates and deasphalting agents contain undesirable components, which are subject to removal: polycyclic aromatic hydrocarbons, heteroatomic asphalt-resin substances, petroleum acids.

By the method of cleaning oils are distinguished as selective, adsorptive, acid-base, acid-contact and hydro-refining.

During cleaning by the selective solvent (fenol, furfural and N- methylpyrrolidone), there are removed polycyclic aromatic compounds, resins, asphaltenes and hetero-compounds, which worsen the viscosity-temperature and antioxidant properties of oils. With the hydro-refining (or contact cleaning) there are removed polar hetero-compounds, which worsen color and odor [8, 9, 10, 11, 36]

The basic indices of quality of lubricating oils are: viscosity level and viscosity-temperature properties, solidification point, chemical stability, lubricating protective and anticorrosive properties. [3, 4, 5, 12, 35]

Isoparaffinic and naphthenic hydrocarbons possess the best viscosity-temperature properties, monocyclic naphthenes, naphthenoaromatic components and high-molecular sulfur compounds are chemically stable. However, aromatic hydrocarbons do not possess analogous properties and they are subject to removal.

Partially synthetic oils are obtained by mixing highly purified mineral base oils with synthetic ones. In comparison with synthetic they have lower cost, a number of deficiencies of synthetic oils is removed in them and the advantages of the latter are preserved.

Motor oils are intended for the lubrication of internal combustion engines (ICE) of different types (carburetor, injection, diesel, turbojet). Their fraction in the total volume of the

production of oils composes 50-60%. Base oils are classified depending on the viscosity index, content of the saturated compounds and technology of production. [13, 30, 33, 34]

The additives to motor oils are multifunctional. Their total quantity in commercial oils reaches 15-20%. Usually motor oil contain the following additives: benzene dispersing (????), detergents (washing additives), acid-proof antiwear, anticorrosive, antifoam, depressive. All-season oils contain viscous (thickening) additives; into energy-saving oils are added antifriction additive – the modifier of friction. For transport simplification, storage and mixing of base oils with additives there are used the packet of additives, into composition of which do not enter only depressor and viscous additives. With a change in the dosage of packet there are obtained oils with different level of performance properties. [14, 15, 16, 17, 18]

1.13 Purpose and Objective

What are we going to do?

It is of interest to obtain new base oils, also to develop the simplified methods of cleaning and regeneration of waste motor oil. Obtained conditioned base oils after the addition of additives acquire commercial properties for application in different branches of technology.

In the process of use of oils they accumulate the oxidation products, pollution and other admixtures, which sharply decrease the quality of oils. Oils, containing the soiling admixtures, are not capable of satisfying the requirements presented to them and must be substituted with fresh oils. Waste oils are collected and are subjected to regeneration for the purpose of retention of valuable raw material, which is to a considerable extent economically advantageous. [19, 20, 21, 22]

The regeneration of the group of waste oils (second treatment) – it is used for the mixture of waste oils. From this raw material it is possible to obtain base oils of different composition and designation. In this case the application of complex processes is assumed: sulfuric acid cleaning, hydro refining, extraction, vacuum distillation and other physical and chemical methods. [39]

Depending on the process of regeneration of the group of waste oils there are obtained 2-3 fractions of base oils, from which by compounding and by the introduction of additives can be prepared commercial oil.

We investigate the types of raw material, their physical and chemical compositions and hydrocarbon composition, modes and conditions of obtaining the end products with the developed technology, obtaining the prototypes of products for the tests, the development of technical-normative documentation, the introduction of products into the production in enterprises, for the joint generalization of the results of research works.

Oils will be received by percolation cleaning on aluminosilicate and two-step hydro refining, at the high temperature and pressure in the presence of catalysts. This oil has high national-economic value, at present it successfully substitutes the utilized imported silicone oils for processing synthetic fibers.

Oils with high degree of contamination and oxidized oils are usually subject to regeneration on special industrial installations. Regeneration includes the physical processing, as a result the suspended and dissolved alien substances, the products of combustion, and also additives are practically completely removed from oils.

Among the different industrial processes of second treatment there are separated groups on a basis of basic method of cleaning: sulfuric acid cleaning, adsorptive cleaning, hydro refining, extraction cleaning, thin-film vaporization, ultrafiltration and other methods.

The average yield of regenerated oil from waste one, containing about 10% of solid soiling admixtures and water, 2-4% of diluted fuel, composes 70-85% depending on the method of regeneration used.

Waste motor oils have low volatility, toxicity, carcinogenicity and are subjected to biodecay.

Toxicity in essence is determined by decomposition of oils during exploitation. To the toxic pollution belong lead antiknock compounds and products of incomplete combustion of fuel in motor oils. Toxic substances can appear during oxidation and nitration at their thermal decomposition. [23, 24, 37]

From ecological and medical points of view there are three fundamental problems connected with waste mineral oils [6, 31, 37]

- appearance of dermatitides, which lead to degreasing of skin, appearance of cracks and introduction of infection in the absence of the means of protection.

- with the sufficient obviousness it is established carcinogenicity of some oil fractions, caused by a number of compounds, which are absent in the fresh products.

Recently there appeared the problem of pollution OMM by the compounds of halogens, connected mainly with the second treatment and utilization.

The consideration of all problems includes the investigation of base oils, spheres and conditions of their application, and also additives.

Dermatological and allergic diseases in essence are caused by waste petroleum oils, and also, in particular, this is caused by the complication of their composition.

In the contemporary technical literature in the study of the problems of regeneration of the quality of waste oils there are used different terms – cleaning, regeneration and second treatment. In this connection it should be clearly demarcated the designation and the fields of application of these processes, achieved by help of sumps, filters, centrifuges and adsorbers. Similar measures contribute to the prolongation of the period of service of lubricants.

Regeneration accomplishes reduction of the quality of individual, completely waste lubricant to the level of fresh. In this case the properties of waste oils are completely reduced, which are used again according to the straight designation. For conducting the regeneration there are used more complex physical and chemical processes – coagulation, sulfuric acid and adsorptive cleaning.

In the case of the treatment of mixtures of different oils it is used the method of second treatment, which assumes the application of a complex of processes – minimum double vacuum distillation, extraction, hydro refining, etc.

Among the contemporary methods of cleaning and regeneration predominate physical methods – deposit, centrifuging, filtration, vacuum drying. [25, 26, 27, 28]

Among the industrial processes of second treatment it must be marked the groups using the basic method of cleaning: sulfuric acid, adsorptive, hydro refining, extraction, thin-film vaporization. the combined process with utilization of a chemical method of demetallization of waste oils is considered separately. Among these processes the basic are:

- acid- contact cleaning:

- acid – contact cleaning, combining atmospheric–vacuum distillation.

Recently, with increase in the content of additives in oils during the acid –contact cleaning it is raised the expenditure of acid and sorbents, which is undesirable.

The modified versions of the process of acid-contact cleaning, which include the stage of heat processing of raw material, which facilitates reduction in the consumption of acid, are used in many countries. In this case oil liberation comprises about 66% of mass. In certain cases acid – contact cleaning is used in combination with vacuum distillation, processing by furfural and by sorbents. at present it is conducted the work on creation of acid-free processes. [8, 9]

Sufficiently stable and high quality base oils are obtained with utilization of adsorptive cleaning (contact or percolation method) as a basic stage. Base oils are mixed with fresh oils and there are added additives.

Deficiencies of the technology consist in the absence of the control of viscosity and the limit of boiling of the obtained product, in the significant losses of oil with sorbent. Certain difficulties appear with the need of utilization of large quantities of waste sorbent.

Deficiencies in the method are partially removed by introducing into the scheme the vacuum distillation of raw material.

Alternative to adsorptive cleaning are hydrogenation processes; however, in this case sorbents are necessary for the protection of the catalysts of hydro refining from premature deactivation by metals and resinous compounds.

The known at present industrial processes with utilization of hydro refining are combined usually with the vacuum distillation. In a number of cases hydrogenation processes are used for the final purification of purposeful converted products. Hydro refining is combined with extraction by propane.

The very promising process of second treatment of motor oils is thin-film vaporization (TFV). Rotary vaporizer finds the greatest practical application.

In a number of countries work the installations of the process, basic stages of which are atmospheric and vacuum distillation, high-vacuum thin-film vaporization, hydro refining and fractionation. The process makes it possible to handle waste motor oil with obtaining of components up to 60-65%, and the general output of useful products is 95%. Remainder can be used as fuel or the component of asphalt.

The process, which assumes the one-time vaporization of raw material, vacuum distillation, two-step distillation in thin-film vaporizers and hydro-cleaning with subsequent processing of oil by hydroxide of sodium, is used. The high quality of end product, identical to fresh oil, is an advantage. Good ecological properties make it possible to use also for suppression of the formation of dust on the roads.

Among the processes used in industry the technology, where during the first stage it is conducted the demetallization of waste motor oil by the solution of diamoniifosfata, is remarkable. After filtration oil is being hydro-cleaned. The advantage of process is the possibility of obtaining commercial motor oil on the base of target products without addition of fresh oils.

Within the framework of the project it will be executed the following basic works:

- from the low-sulfur oils of Georgia and Azerbaijan it will be isolated wide oil fraction;
- the wide oil fraction by repeated rectification will be divided into the narrower light, average and heavy fractions;
- the fractions will undergo the thorough percolation cleaning for the purpose of obtaining base oils;
- it will be refined selective functional additives;

- compounding by the chosen additives of base oils for the purpose of obtaining motor oils;
- the identification of the parameters of motor oils by contemporary instrument methods;
- tests of motor oils for the intensity of the wear of metals;
- tests of base oils instead of (58-60%) silicone liquid in the lubricant for the formation of fibrous threads;
- tests of base oils as non-blocking agent in aerosol containers (instead of silicone liquid), used in molds during the extrusion of parts made of plastics;
- the regeneration of the mixtures of waste motor oils to base oils;
- the compounding of regenerated oils with the chosen additives;
- the identification of the parameters of regenerated and on their basis motor oils: - testing commercial motor oils for the intensity of the wear of metals.

What's the objective?

The contemporary internal combustion engines of different construction impose on petroleum base and motor oils the most important operational and ecological requirements.

For this purpose in the represented project it is examined obtaining petroleum base oils from Georgian and Azerbaijan oils. Oils, obtained by the deep repeated vacuum distillation of oil and thoroughly cleaned by the percolation method will be used in two directions:

1. As the substitute of sharply deficient and expensive silicone liquid, basic component (58-60 %) of lubricant at the formation of synthetic and artificial fibrous threads; as non-blocking agent in the aerosol containers, used in molds, during the extrusion of technical articles made of plastics, where the special interest is preparation radio parts of military designation.

2. The quantities of specific, easily accessible and cheap additives for compounding by them of purified base oils with obtaining of motor oils will be simultaneously established. The parameters of motor oils will be established by contemporary instrument methods and practical wear tests of metals.

3. Besides obtaining of petroleum base and motor oils, it is investigated the regeneration of waste motor oils of the internal combustion engines to the level of fresh for the purpose of their again application. Regenerated oils will be compounded with additives of functional designation chosen by us beforehand.

The target of project is extremely urgent from the ecological and economic point of view. The utilization of base and motor oils will ensure the protection of environment from different pollution. Concerning economic side, it suffices to give the example of replacement of one tones of silicone liquid with the same quantity of petroleum base oil in the lubricant and in the aerosol containers, which in this case will give significant economic effect expressed by several thousand dollars.

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1.14 Expected Significance

What's new?

As a result of the project it will be realized production of base and motor oils by a deep repeated vacuum distillation of petroleum. Oils will satisfy contemporary requirements by operational, ecological and economic characteristics.

Waste motor oils will be regenerated to the level of fresh, for application according to the designations.

By the technology developed by us petroleum base oil, which will replace silicone liquid in the lubricant at formation of fibrous threads and non-blocking agent in the aerosol containers for the extrusion of technical details made of plastics.

Potential consumers of the developed technology will be state and private companies, which deal with the similar developments.

The methods of study are in accordance with target and problems of the project.

The base material in the performing of work will be: 1) utilization of additives for the purpose of compounding base oils in motor oils

2) replacement of silicone liquid by base oils in the lubricant with formation of fibrous threads and non-blocking agent in the aerosol packing for molds during the extrusion of technical details from plastic masses;

3) regeneration of waste motor oils to the level of fresh aiming at their repetitive application.

1.15 Organization, Qualification and Staffing

Who are we?

The workers of GTU (Georgia, Tbilisi) and the Institute of "Petrochemical processes" of Baku (Azerbaijan), which participate in the project, have long-standing qualification acquired in the flow of ten-year work experience in laboratories and practice. This is confirmed by publications and reports at international conferences.

The participants of the project know Russian, English and French.

1.16 Expected Results

What will be done in the framework of this project?

In the case of successful completion of the planned experiments:

Production of base and motor oils;

Application of base oils instead of expensive and sharply deficient silicon liquid in the production of synthetic

fibers and non-blocking agent for the extrusion of parts made of plastics, and also regeneration of waste motor

oils to the level of fresh will create precedents in the development of contemporary deep petroleum refinement.

It is planned to introduce the developed technology of production of base and motor oils into free market.

1.17 Scope of Activities

How will the investigation be organized?

For fulfilling the works planned by the project we will isolate butyric wide fraction from the low-sulfur oils of Georgia and Azerbaijan within the limits of temperature of boiling 350-500 °C.

- the wide oil fraction will be the subject to fractionation to the narrower (light, average and heavy) fractions;
- the narrow fractions will be the subject to the thorough percolation cleaning for obtaining base oils;

Besides percolation cleaning the fractions of aromatic hydrocarbons we will apply the method of two-step hydrogenation. Two-step hydrogenation was conducted at a pressure and high temperature in the presence of aluminosilicate and industrial catalysts. The utilized method will make it possible to obtain naphtheno-paraffin oil without the loss of source material.

- selection of selective functional and active additives for compounding by them base oils;
- identification of the parameters of obtained motor oil, its testing in the process of friction and wear of metals;
- testing base oils as the basic component of lubricant instead of silicone liquid with formation of synthetic and artificial fibrous threads;
- testing base oils as non-blocking agent in the aerosol containers instead of silicone liquid in the molds during the extrusion of technical details made of plastics for different designation;
- regeneration of the waste mixtures of motor oils to the level of fresh for their repetitive application;
- processing of the regenerated oils with additives for obtaining motor oils.
- identification of the parameters of obtained motor oils and their testing for intensity of the wear of metals.

1.18 Technical Methodology

How will the science be done?

The methods of study are in accordance with the target and problems of the project.

The base material in the performing of work will be: 1) utilization of additives for the purpose of compounding base oils in motor oils

2) replacement of silicone liquid by base oils in the lubricant with formation of fibrous threads and non-blocking agent in the aerosol packing for molds during the extrusion of technical details from plastic masses;

3) regeneration of waste motor oils to the level of fresh aiming at their repetitive application.