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REVIEWS

UTILIZATION OF SPENT LUBE OILS

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Oxidation products, contaminants, and other impurities accumulate in oils in the process of their use, drastically impairing the oil quality. Such oils cannot meet the specified requirements and must be replaced by fresh ones. Spent oils are collected and regenerated to conserve this valuable material, which is economically useful. In the territory of the former Soviet Union, about 1.7 million tons of spent oils are collected every year, out of which up to 0.25 million ton, i.e., 15%, is refined. Refining of spent lube oils (SLO) along with crude oil in refineries is not possible as they contain additives that impair the operation of the process equipment.

The ways of utilizing SLOs are as follows:

- cleaning and regeneration;
- thermal degradation (burning);
- making plastic lubricants for preservation;
- lubricating noncritical machine parts and mechanisms;
- production of building materials.

Depending on the regeneration process, from the spent oils can be obtained two-three base oil fractions, from which commercial oils (engine, transmission, hydraulic, etc.), lubricating-cooling fluids (LCF), plastic lubricants, etc. can be produced by compounding and introducing additives. The average yield of regenerated oil from the spent one containing about 2-4% solid contaminants, water, and up to 10% fuel is 70-85%, depending on the regeneration method.

In order to remove aging products and contaminants from the oils and to restore the properties of the oils, physical, physicochemical, and chemical methods are used. These methods involve application of more sophisticated equipment and large expenditures.

The *physical methods* allow removal from the oils of solid contaminant particles, microdrops of water, and partially resinous (gummy) and carbonized substances. These methods include treatment of the oil in a force field using gravitational, centrifugal, and, less commonly, electrical, magnetic, and vibratory forces, filtration, washing with water, evaporation and vacuum distillation, and various mass- and heat-exchange processes, which are used to remove from the oils hydrocarbon oxidation products, water, and low-boiling fractions.

Sedimentation is the simplest method, being based on natural settling of mechanical particles and water under gravity. Depending on the degree of contamination of the fuel or oil and the cleaning time, it is used either

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as an independent or as a preliminary method preceding filtration or centrifugal cleaning. The major flaws of the sedimentation method are long duration for complete settling of particles and removal of only the large particles measuring 50-100 mm.

In order to remove mechanical particles and gummy (resinous) substances by filtration, the oil is passed through screen or depth filtering diaphragms (membranes). Metallic and plastic screens, glass wool, fabric, paper, composite materials, and ceramics are used as filter materials. In many organizations using lube oils, for raising the quality of cleaning of these oils, the number of filters for rough (primary) cleaning is increased and a second stage of fine (thorough) cleaning of the oil is introduced into the technological process.

In [1], a description is given of the use of metallic filters made of superfine molybdenum or tungsten fibers. The multilayer filter is capable of efficiently cleaning up to 5000 liters of SLO, and can be easily regenerated by igniting, followed by blowing (purging) with compressed air under several atmospheres of pressure.

The most efficient and productive is the method of removal of mechanical impurities and water by centrifuging. This method is based on separation of heterogeneous mixtures into various fractions under centrifugal force. The centrifuge helps remove mechanical impurities from the oils down to 0.005 wt. %, which corresponds to the purity class 13 as per GOST (Federal State Standard) 17216-71, and dehydrate to the level of 0.6 wt. %.

The NITI TESAR (Saratov) technology and equipment are the best known and most popular. This institute has developed a wide range of SOG type of test benches and a line for cleaning LTM type of transformer oils for regeneration of SLOs. The SOG test benches (six modified versions) are provided with a centrifuge that helps remove contaminants to cleaning class 3-7. Also, they are capable of removing undissolved water. Thanks to their compactness and mobility (portability), they can be used right at the working sites near the equipment.

The *physicochemical methods* are in wide use. They include coagulation, adsorption, and selective dissolution of the contaminants contained in the oil. Ion exchange cleaning is a modified version of adsorption cleaning.

The efficiency of the coagulation process depends on the amount of coagulant added, duration of its contact with the oil, temperature, stirring efficiency, etc. Coagulation of the contaminants in the spent oil generally takes 20-30 min, after which the oil can be cleaned from the enlarged contaminants by precipitation, centrifuging, or filtration.

Adsorption cleaning of spent oils is based on the ability of adsorbents to retain the products contaminating the oil on the outer surface of the granules and the inner surface of the capillaries that pierce the granules. Natural (bleaching clays, bauxites, natural zeolites, etc.) and synthetic (silica gel, alumina, aluminosilicates, synthetic zeolites, etc.) substances are used as adsorbents.

Adsorption cleaning can be accomplished by contact method that consists in stirring the oil with ground adsorbent, percolation method where the oil is passed through the adsorbent, and countercurrent method in which the oil and the adsorbent move in opposite directions. One of the demerits of the contact cleaning method is that it requires a large quantity of adsorbent that pollutes the environment. In percolation cleaning the adsorbent is usually silica gel, which renders this method costly. The most promising is the method of cleaning oil in a moving adsorbent bed, which makes the process continuous, without interruption for periodic replacement, regeneration, or filtration of the adsorbent. But this method requires fairly complicated equipment, which deters its wide use.

Ion exchange cleaning is based on the ability of ion-exchange resins to retain contaminants that dissociate in dissolved state into ions. Cleaning can be achieved by the contact method by stirring the spent oil with 0.3-2 mm ion-exchange resin granules or by the percolation method by passing the oil through a column packed with ion-exchange resin. Thanks to ion exchange, the mobile ions in the spatial lattice of the ion-exchange resin are replaced by ions of the contaminants. The properties of the ion-exchange resins can be restored by washing the resins with a solvent, followed by drying and activation with 5% caustic soda solution. Ion exchange cleaning can be used for removing acidic contaminants from the oil but not for retaining resinous (gummy) substances.

Selective cleaning of spent oils is based on selective dissolution of individual oil-contaminating substances: oxygen-, sulfur- and nitrogen-bearing compounds, and, where necessary, polycyclic hydrocarbons having short side chains which impair high-temperature properties of oils.

Selective solvents used are furfural, phenol, its mixture with cresol, nitrobenzene, various alcohols, acetone, methyl ethyl ketone, etc. Selective cleaning can be carried out in mixer-settler type of apparatuses in combination with vaporizers for distilling off the solvent (step-by-step extraction) or in two columns (an extraction one for removal of the contaminants from the oil and a fractionating one) for distilling off the solvent (continuous extraction). The second method is more economic and more popular.

A modified version of selective cleaning is treatment of the spent oil with propane, whereupon the hydrocarbons dissolve in the propane and the resinous-asphaltenic substances present in the oil in colloidal state precipitate out.

The *chemical methods* of cleaning are based on reaction between the substances that contaminate the spent oils and the reagents that are added to these oils. As a result of the reactions, compounds easily removable from the oil are formed. The chemical methods include acid and alkali treatment, oxidation with oxygen, hydrogenation, and drying and removal of contaminants using oxides, carbides, and hydrides of metals.

Processes using sulfuric acid occupy the first place in the world in number of installations and volume of feedstocks treated. Acid cleaning produces a large amount acid sludge, which is not easily utilizable and is an ecologically harmful waste. Furthermore, sulfuric acid cleaning is not suitable for removal from spent oils of polycyclic aromatic hydrocarbons and highly toxic chlorine compounds.

Hydrogenation processes are being used increasingly in spent oil cleaning. The reason for this is wide scope of these processes for getting high-quality oils, and they are ecologically much cleaner than sulfuric acid and adsorption cleaning processes.

The installation for hydrofining of oils is generally integrated with a suitable crude oil refinery having surplus hydrogen and provision for recycling it.

In order to rid spent oils of polycyclic compounds (resins), highly toxic chlorine compounds, oxidation products, and additives, use is made of processes where metallic sodium is used. Polymers and sodium salts with a high boiling point formed in these processes make it possible to distil off the oil. The yield of cleaned oil exceeds 80%. The process does not require elevation of pressure and use of catalysts and is not associated with formation of hydrogen chloride and hydrogen sulfide. A few of such installations operate in France and Germany. Among the industrial processes where metallic sodium suspension in petroleum oil is used, the best known are the Recyclon process (Switzerland) and Lubrex process (Switzerland) that uses sodium hydroxide and bicarbonate. These processes can be used to clean any spent oils with a desired product yield of as high as 95%.

Spent oils can be regenerated by a variety of apparatuses and equipment whose operation is generally based on the use of a combination of methods (physical, physicochemical, and chemical), which allows regeneration of spent oils that differ in types and have quality indices reduced to varying degrees.

Note that in the process of regeneration of oils we may get base oils, which are identical to fresh ones in quality, with yields of 80-90%, depending upon the feedstock quality. Thus, base oils can be regenerated at least two more times, but such regeneration is possible only if modern technological processes are used.

One of the problems that drastically reduce the economic efficiency of SLO utilization is high cost of collection, storage, and transportation to the refining site.

Construction of mini-complexes for oil regeneration to meet requirements of small territories (territory, region, or city with a population of 1-1.5 millions) will ensure reduced transportation costs, and output of high-quality end products (lube oils and lubricating greases) will bring such mini-complexes closer in economic efficiency to production of these products from crude oil.

Transformer oils are regenerated in UVM, UOM-100, and other installations [2]. The principle of operation of these installations is based on centrifugal cleaning on an SOG bench, followed by adsorption cleaning and drying with zeolites and silica gel.

Thermal degradation (burning) is the most popular and demanded way of utilizing SLO. A minor part of SLO is burned in ill-equipped boilers and furnaces and the major part is discharged into waterways, sewerage, and soil, and even sprayed into the atmosphere causing inestimable ecological damage. Only 10% of SLO is used by the chemical industry, for example for manufacturing little-used plastic lubricants and second grade oils which are also utilizable.

However, SLOs are a high-calorie fuel. This resource should be used maximally in situ for heat and power generation, the more so because modern technology makes it possible to burn it in efficient and ecologically clean way.

The heat of combustion of SLO is greater than that of coal, diesel oils, and residual fuel oils. It exceeds 41.9 MJ/kg, which represents a high heat energy value.

In Russia, the volume of SLO as a conventional fuel is as much as 10 million tons/yr, which corresponds to 293.3 million GJ of heat (81.4 BWh).

Spent oils are used for operating many furnaces and units built both domestically, e.g., T-603, ZhAR-25, AKULA, EKOM, and UM-KA, and abroad, e.g., MASTER (USA), KROLL (Germany), W401L, WA29A, WA59A, R&K-140B (Italy), THERMOBILE (Holland), CLEAN BURN (USA).

Installations for preliminary production of water-fuel emulsions, for example the reactor USMOR-08 (Belarus) and hydrodynamic siren SGD-3G (Zlatoustovsk Machine Building Plant), ensure high-quality burning of SLO.

The All-Russia Scientific Research, Design, and Technology Institute for Use of Equipment and Petroleum Products (VIITiN) proposed and tested with favorable results several conserving (protective) materials based on SLO for protecting farming machinery from corrosion [3, 4].

The test results showed that materials produced from easily available waste petroleum products could be used to protect farming machinery. Compositions based on SLO have high protective capacity. The technological parameters of the protective materials can be improved by adding to them up to 10 wt. % of diesel oil and 5 wt. % of emulsifying agent or residue (dregs) of sunflower oil (to improve adhesive properties).

Sometimes SLOs are used for lubricating secondary (noncritical) parts of machines and mechanisms. Their use for lubrication of metal molds in production of precast reinforced concrete is well known. Further, SLOs are used for lubricating metallurgical powders in steel works, as a lubricating material in foundry, and for treatment under pressure.

Oftentimes SLOs are used as hydraulic fluid in the hydraulic system of garbage trucks.

Methods of SLO use in production of certain building materials are interesting and promising. For example, one of these is based on the properties of oxides of mineral sorbents for quenching (extinguishing) to increase the specific surface 15-30 times and to turn thereupon into volume binder with a high absorption capacity.

Spent lube oils are treated with the preparation EKONAFT-M [TU 5744-001-11085815-2005] in a specially designed mixer. As a result of the reactions, the preparation adsorbs petroleum products uniformly with production of a dry, powdery substance, which is a petroleum waste utilization product. This product consists of minute granules representing microparticles of petroleum oil wastes enclosed in calcareous capsules, which are evenly distributed in the product.

A technology has been developed for utilization of SLOs along with wastes of polymeric materials and polymeric-bituminous binders obtained thereof.

In [5, 6], a method has been proposed for utilization of spent mineral oil through its use in a feedstock mix for manufacture of bricks. To get the mix, granulated Cherepovets slag is mixed with spent mineral oil in the 1:10 ratio and added to clay in the amount of 20 wt. %. The brick cast from this mix is kilned in an oxidizing atmosphere at 960-1000°C, holding it at the maximum temperature for at least one hour.

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