

presence of a tertiary amine group in its molecule. A weak stabilizing effect is observed for the Agidol-12, which is a blend containing a certain amount of the MBI.

Effective stabilizing additives may be formulated from phenolic antioxidants and certain special-purpose additives, particularly dispersants. Preliminary tests have indicated excellent possibilities in working along these lines (see Table 4, Samples A and B). The additives can be formulated from components produced commercially in the USSR.

LITERATURE CITED

1. M. W. Schrepfer, R. J. Arnold, and C. A. Stansky, *Oil Gas J.*, 82, No. 3, 79-84 (1984).
2. K. Kanariev, A. Ivanov, and Z. Kutsarova, *Khim. Ind. (Sofia)*, 58, No. 8, 346-348 (1986).
3. A. A. Gureev, T. V. Palichev, and D. M. Minkov, *Khim. Tekhnol. Topl. Masel*, No. 10, 12-13 (1987).
4. A. M. Danilov, *Khim. Tekhnol. Topl. Masel*, No. 3, 42-44 (1987).
5. A. A. Gureev, E. P. Seregin, and V. S. Azev, *Qualification Test Methods for Petroleum Fuels [in Russian]*, Khimiya, Moscow (1984).
6. G. F. Bol'shakov, *Physicochemical Principles of Precipitate Formation in Jet Fuels [in Russian]*, Khimiya, Moscow (1972).
7. A. A. Gureev and G. B. Prigul'skii, *Khim. Tekhnol. Topl. Masel*, No. 6, 16-18 (1985).
8. F. R. Mayo and B. Y. Lan, *Ind. Eng. Chem., Prod. Res. Dev.*, 25, No. 2, 333-348 (1986).

TREATMENT OF POLYMER-COMPOUNDED HYDRAULIC OILS BY ULTRAFILTRATION

V. A. Kulikova, A. I. Bukhter, L. K. Davidyan,
G. S. Krasnov, and Yu. A. Avdonin

UDC 66.067:665.544

Polymer-compounded oils have been finding more and more applications in the lubrication of components of vehicles and mechanisms, and also as the working fluids in various hydraulic systems. These products are formulated from a low-viscosity oil base plus polymeric additives such as polymethacrylates, Oktol [low-molecular-weight polybutylenes], Vinipol [poly(vinyl n-butyl ether)]. Such oils are characterized by good viscosity-temperature properties at low and high temperatures. After these oils have been in service for a certain time, they are drained and discarded as unsuitable for further use.

There is no economic commercial method for reclaiming polymer-compounded oils. One method of oil reclaiming is treatment with sulfuric acid followed by neutralization. However, this results in the formation of large amounts of waste materials that present a problem in environmental pollution. Oil reclaiming by such methods as deasphalting, vacuum distillation, hydrotreating, or contact-treating with bleaching clay is quite complex and costly in terms of energy requirements and capital investment [1].

In many branches of industry, treatment methods using polymeric membranes have come into use. The principles of membrane separation technology are described in [2]. According to data reported from other countries [3], ultrafiltration using "nuclear" membranes is one of the promising methods of oil reclaiming. The mechanical design of equipment for this process is simple, the energy costs are low, and, as a consequence, the process is very economical. Distinctive features of nuclear membranes are the regular cylindrical form of the pores and the extremely narrow size distribution of the pores [4].

We have applied ultrafiltration to the reclamation of used AMG-10 oil. This oil is intended for operation at ambient temperatures from -66°C to +55°C. It is prepared from a low-viscosity, low-power petroleum base stock (a distillate produced from the kerosine cut of Balakhany crude by severe treatment with sulfuric acid) plus a polymeric V. I. improver, an antioxidant, and a dye. The V. I. improver is Vinipol VB-2 (a polymer of vinyl butyl ether with a molecular weight of 15,000-20,000). The base stock of the AMG-10 oil has a viscosity

Ryazan' Pilot Plant, All-Union Scientific-Research Institute for Petroleum Processing. dzerzhinsk Branch, State Scientific-Research and Design Institute of the Nitrogen Industry and Products of Organic Synthesis. Translated from *Khimiya i Tekhnologiya Topliv i Masel*, No. 11, pp. 11-13, November, 1989.

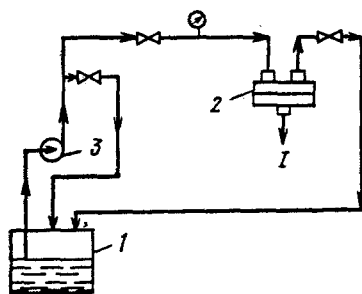


Fig. 1. Diagram of laboratory ultrafiltration unit for cleanup of used oil: 1) oil tank; 2) membrane filter holder; 3) oil pump; I) filtrate.

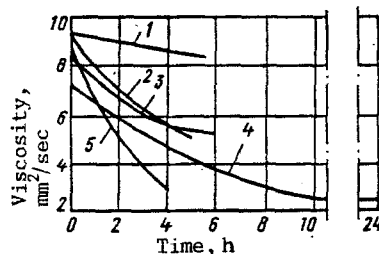


Fig. 2. Change in viscosity of AMG-10 oil during operation of unit on indicated membranes: 1) polyurethane (pressure $p = 0.2$ MPa, permeability $\Pi = 3.7$ liters/h·m²); 2) polyvinyl chloride ($p = 0.2$ MPa, $\Pi = 2$ liters/h·m²); 3) polysulfonamide ($p = 0.5$ MPa, $\Pi = 0.3$ liter/h·m²); 4) polyethylene terephthalate ($p = 0.5$ MPa, $\Pi = 8$ liters/h·m²); 5) polyacrylonitrile ($p = 1.2$ MPa, $\Pi = 3.2$ liters/h·m²).

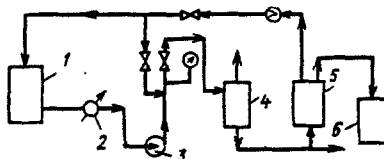


Fig. 3. Diagram of pilot-plant unit for treatment of oil by ultrafiltration: 1) oil tank (volume 3 m³); 2) water-cooled exchanger; 3) centrifugal pump with capacity up to 30 m³/h; 4) coarse filter; 5) membrane apparatus with modular block of plane-parallel membrane elements; 6) treated oil receiver.

of 2.3-2.4 mm²/sec at 50°C; after compounding with the Vinipol, the oil has a minimum viscosity of 10 mm²/sec at 50°C. When the oil is in service, the Vinipol molecules breakdown, and the oil viscosity drops to the level at which it is discarded, 7.5 mm²/sec.

The permeability and selectivity of membranes in cleanup of AMG-10 oil were investigated in laboratory and pilot-plant units. The laboratory unit (Fig. 1) consisted of an oil tank, a membrane filter housing, a nitrogen tank for operation without recirculation, and an oil pump for operation with recirculation. The working surface of the membrane in the holder was 42 cm². In the experiments, the temperature was varied from 15° to 50°C.

In the selection of the membrane, we investigated porous films of polyurethane, polyvinyl chloride, polysulfonamide, Lavsan (nuclear filters based on polyethylene terephtha-

TABLE 1

| Filtration stage | Pressure, MPa | Permeability, liters/(h·m ²) | Oil viscosity, mm ² /sec | |
|---|---------------|--|-------------------------------------|-----------------|
| | | | original | after treatment |
| Polyacrylonitrile membrane (pore diameter 0.8 μm) | | | | |
| 1 | 3,0 | 0,5 | 7,44 | 3,76 |
| 2 | 0,2 | 6,3 | 3,76 | 2,63 |
| 3 | 0,1 | 13,0 | 2,63 | 2,44 |
| Lavsan membrane (pore diameter 0.5 μm) | | | | |
| 1 | 0,2 | 3,2 | 10,30 | 3,22 |
| 1 | 0,3 | 4,4 | 9,70 | 2,70 |

late), and polyacrylonitrile. The membrane efficiency was determined on the basis of the viscosity of the treated oil, which characterizes indirectly the degree of removal of the thickening agent (V. I. improver) from the base stock.

The results from these studies (Fig. 2) showed that the Vinipol thickening agent is most completely removed by the use of the Lavsan and polyacrylonitrile membranes, with which the viscosity of the treated oil was 2.4 and 3.2 mm²/sec, respectively. In both the laboratory and pilot units, it was noted that the final result of the oil treating operation is influenced not only by the membrane material (Fig. 2), but also by the accumulation of a coating on the membrane surface. As this layer accumulates, the degree of cleanup [removal of the polymer] increases but the permeability drops off on account of the additional hydraulic resistance to liquid flow.

Filtration of the oil through the polyacrylonitrile membrane in three stages gives a filtrate with a viscosity of 2.4 mm²/sec at 50°C, i.e., a filtrate that is practically free of the Vinipol (see Table 1). In the first stage of filtration, the permeability of the membrane is low, probably because of pore plugging by particles of contaminants in the oil; in the second and third stages, the possibility is much higher. When using the Lavsan film (nuclear filters), single-stage filtration gives a filtrate with a viscosity of 2.7-3.2 mm²/sec.

In making a selection of membranes, the Lavsan is to be preferred. The polyacrylonitrile membranes require special conditions of storage in a moist medium and an additional treatment with solvents (acetone and naphtha) before use. The laboratory test results were confirmed in a pilot unit (Fig. 3) that was installed at the Ryazan' Pilot Plant of VNII NP [All-Union Scientific-Research Institute for Petroleum Processing].

The vessel with a modular block that was used as a section of the pilot unit was originally developed for wastewater treatment. So as to adapt this equipment to use on petroleum products, experiments were performed on the selection of a chemically resistant drain material for use as a substrate under the membrane, and also studies to choose a design for the vessel and moduli, the material for the seals between the elements, and the method of sealing-in the membranes when the elements were assembled in the modular block. The material of the supports and the design of these supports have a considerable influence on the dimensions of the channels through which the filtrate is drawn off under the membrane into the receivers; the effects are particularly significant if the material swells when exposed to solvents.

In selecting the drain device, we tested supports made of porous Miplast, Viniplast VN-10 [rigid PVC], and polystyrene. The best results in terms of removing the thickening agent from the AMG-10 oil were obtained on filter elements with drain plates made of polystyrene. However, the polystyrene and Miplast plates soften and become brittle after extended use. Moreover, the Miplast swells, creating a high resistance to flow of the filtrate, with a considerable decrease in permeability. The Viniplast is the most resistant to this particular medium. Further tests showed that, when using a Lavsan membrane with a Viniplast support, 70% of the thickening agent is removed from the used AMG-10 oil in a single stage of filtration, thus confirming the results obtained in the laboratory studies.

The filtrate contains residual amounts of the Vinipol and also products of oil oxidation and Vinipol decomposition that are not retained by the membrane. In order to produce reclaimed base stock for the AMG-10 oil that will meet the requirements imposed on the fresh base stock, it is necessary to treat the filtrate with concentrated sulfuric acid at a rate of 2-3% by weight, as compared to 20% in the conventional treating scheme. This means that

the use of ultrafiltration will give substantial reductions in the quantities of acid sludge and spent caustic that are formed - sixfold and twofold reductions, respectively.

The quality of the oil treated by means of ultrafiltration, after the incorporation of additives, meets the physicochemical property requirements of GOST [All-Union State Standard] 6794-75. In plants producing hydrogen-rich gas, the final treatment of the filtrate may be performed on alumina-cobalt-molybdenum catalyst at 300-350°C under a pressure of 4-5 MPa, with a feedstock space velocity up to 2 h⁻¹, with a feed of hydrogen-rich gas amounting to 300-500 m³/m³. With such treatment, all problems of waste product utilization are eliminated.

LITERATURE CITED

1. A. D. Misnikevich, Reclamation of Used Oils in the USSR and Other Countries [in Russian], in Series: Maintenance of Plants and Facilities, NIITÉkhim, Moscow (1987).
2. V. P. Dubyaga, L. P. Perepechkin, and E. E. Katalevskii, Polymeric Membranes [in Russian], Khimiya, Moscow (1981).
3. "Chemical et petrochemicals," Jpn. Ind. Technol. Bull., 13, No. 8, 17-19 (1985).
4. P. Yu. Apel', V. I. Kuznetsov, N. I. Zhitaryuk, et al., Kolloidn. Zh., 17, No. 1, 3-8 (1985).