

HYGROSCOPICITY OF SYNTHETIC OILS

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Water in lubricating oils has a detrimental effect on many of the service properties of the oil [1, 2]; hence, oil standards and specifications require that no water be present. However, oils may become contaminated with water during storage, transportation and use. One of the sources of water entry is hygroscopicity of the oil.

In our studies of oil hygroscopicity, we stored 40-ml samples of predried oils in a 100% relative humidity atmosphere for 72 h at $20 \pm 3^\circ\text{C}$, after which the quantity of absorbed moisture was determined. These particular conditions ensure that the oil will be saturated with water. The oils examined were the mineral oils MS-8 and MS-8p; the isoparaffinic oil IPM-10; the dioctyl ester of sebacic acid (DOS); two esters of polyhydric alcohols, one the pentaerythritol ester (PEE) and the other the diethylene glycol ester (DEGE) of a $\text{C}_5\text{-C}_9$ cut of synthetic fatty acids; the synthetic oils VNII NP-50-1-4f, VNII NP-7, 36/1 KU-A, B-3V, and non-Soviet oils conforming to the U.S. specifications MIL-L-7808G and MIL-L-23699B.

From the data obtained on these oils (Table 1), it can be seen that synthetic oils based on esters, in contrast to mineral oils, have a greater tendency to absorb moisture from the air. However, among the group of synthetic oils, the hygroscopicity varies over rather wide limits, depending on the nature and structure of the base stock. Of the Soviet commercial oils, the most hygroscopic is the 36/1 KU-A, which contains DEGE. The presence of functional additives gives very little increase in the hygroscopicity of the commercial oils. The hygroscopicity of synthetic oils depends to a greater degree on the structure of the base stock, or, more precisely, on the presence of unesterified hydroxyl groups in the ester molecules.

The results from determinations of the hygroscopicity of PEE and B-3V oil with various degrees of esterification (Table 2) show that as the hydroxyl number of the PEE or the B-3V oil increases, the hygroscopicity also increases quite significantly (1.1% with a hydroxyl

TABLE 1

Oil	Oil type	Hygroscopicity, % water
Bis(2-ethyl hexyl) ester of sebacic acid	—	0.19
Ester of pentaerythritol and $\text{C}_5\text{-C}_9$ SFA	—	0.45
Ester of diethylene glycol and $\text{C}_5\text{-C}_9$ SFA	—	0.98
MS-8	Mineral	0.005
MS-8p	Mineral	0.009
IPM-10	Isoparaffinic	0.005
VNII NP-50-1-4f	Diester	0.20
B-3V	Based on PEE	0.48
36/1 KU-A	Based on PEE and DEGE	0.70
Turbine Oil 325 (MIL-L-7808G)	Diester	0.25
Turbine Oil 500 (MIL-L-23699B)	Neopentyl	0.35

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TABLE 2

Test sample	Hydroxyl number, mg KOH/g	Hygroscopicity, % water
PEE		
1	0,6	0,25
2	6,3	0,30
3	24	0,42
4	106	1,10
B-3V		
1	8	0,35
2	25	0,45
3	60	0,89

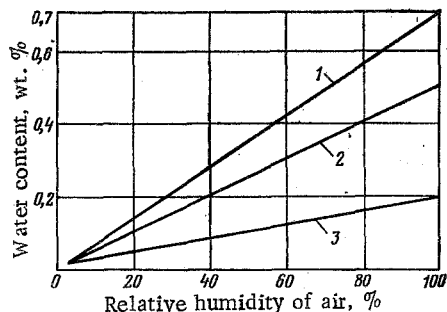


Fig. 1

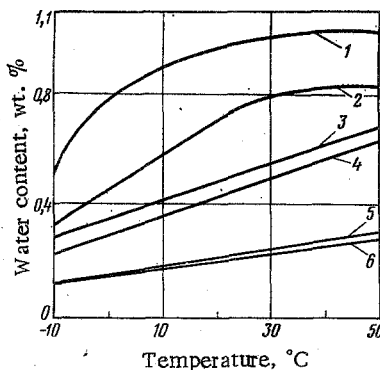


Fig. 2

Fig. 1. Oil hygroscopicity as a function of relative humidity of air: 1) 36/1 KU-A; 2) B-3V; 3) VNII NP-50-1-4f.

Fig. 2. Oil hygroscopicity as a function of temperature: 1) DEGE; 2) 36/1 KU-A; 3) B-3V; 4) PEE; 5) VNII NP-50-1-4f; 6) DOS.

number of 106 mg KOH/g). The hydroxyl number of commercial samples of B-3V oil is about 25 mg KOH/g, and this determines its hygroscopicity, which is 0.45-0.50%. This means that in order to reduce the hygroscopicity of synthetic oils based on esters, the esterification process must be brought nearer to completion.

The capability of hydrocarbons for absorption and dissolution of water depends not only on the chemical structure of the hydrocarbons, but also on the relative humidity of the air and the temperature [3, 4]. The content of dissolved water in fuels and individual hydrocarbons at a given temperature is directly proportional to the relative humidity of the air. Since the solubility of water in esters is several orders of magnitude greater than the solubility of water in aromatic hydrocarbons, it has been a matter of practical interest to investigate the solubility of water in ester-based synthetic oils in relation to the relative humidity of the air and the temperature. Here we define the "solubility" of water in synthetic oils as their hygroscopicity at a given temperature and relative humidity.

The reliability of the results in such studies is very much dependent on the accuracy and rapidity of the methods used to determine the water content. An analysis of the existing methods has shown that the most widely used is the Karl Fischer method in various modifications [5, 6]. In some countries, this method has been adopted as a standard method for monitoring the content of water and petroleum products. For use in our studies, we selected the Karl Fischer method with electrometric indication of the titration end point.

The procedure used in investigating the dependence of oil hygroscopicity on the relative humidity and temperature was the same as that used in evaluating the hygroscopicity at saturation. The variables investigated were the relative humidity of the air and the temperature. The required humidity of the air was established by means of saturated aqueous solutions of mineral salts. The experimental data (Fig. 1) show that regardless of the nature or chemical composition of the oil, the quantity of absorbed water is directly proportional to the relative humidity of the air; i.e., Henry's law is followed.

Thus, if we know the hygroscopicity of the oil as determined at 100% relative humidity, we can calculate its hygroscopicity at any other relative humidity by the use of the equation

$$C = C_{\max} \psi$$

where C is the content of dissolved water, wt. %; C_{\max} is the maximum content of dissolved water at the given temperature (hygroscopicity), wt. %; $\psi = P_w/P_w^{\text{sat}}$ is the relative humidity of the air; P_w is the partial vapor pressure of water at the given temperature; P_w^{sat} is the saturated vapor pressure of water at the given temperature.

The solubility of water is highly dependent on temperature [3, 4]; for many pure hydrocarbons, this relationship is expressed by the equation [3] $C = a - (b/T)$, where C is the solubility of water in the hydrocarbon at temperature T , wt. %; a and b are coefficients that are constant for any given hydrocarbon; T is the temperature, °K.

In our experiments, as the temperature was increased from -10° to 50°C , the hygroscopicity of the esters and oils based on these esters was found to increase (Fig. 2). The character of these relationships in the range of temperatures investigated was different from the logarithmic dependence that has been found for hydrocarbons with low water solubility. For diesters and PEE, the water solubility is directly proportional to temperature. In the DEGE and 36/1 KU-A oil, the increase in water solubility as the temperature is increased is less pronounced than in the DOS or PEE.

These relationships between the solubility of water in synthetic oils and the temperature can apparently be explained as follows. In hydrocarbons, with a low water solubility, the main factor in the solubility is physical "implantation" of water molecules between hydrocarbon molecules, which is determined mainly by the temperature of the hydrocarbon. In the highly polar esters, the solubility of water is determined mainly by its interaction with the polar molecules of the ester through the formation of hydrogen bonds, and the product temperature is a less important factor. Therefore, when the temperature is increased, the solubility of water in esters already containing a considerable amount of dissolved water does not increase to as great a degree as is observed in petroleum hydrocarbons.

Thus, synthetic oils are considerably more hygroscopic than mineral oils. The hygroscopicity of synthetic oils based on esters increases with increasing relative humidity of the air and with increasing temperature. As the degree of esterification is increased, the hygroscopicity of PEE drops off considerably. In storage and use of these oils, all possible contact with the atmosphere must be eliminated, particularly under conditions of high humidity and temperature.

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