Investigation of the possibility of using coagulant for cleaning used motor oils

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Abstract. The article is devoted to studying the possibility of using organic or inorganic coagulants in the process of purification of used motor oils (UMO). In experimental studies, combinations of aqueous solution of carbamide, acetic acid and isopropyl alcohol were used as coagulants. The analysis showed that the third variant of coagulant combination was the most effective. Mathematical models were obtained. Varying factors: percentage of coagulant \( \alpha \) (%), settling temperature \( t \) (°C) and settling time \( \tau \) (min\(^{-1}\)). The mathematical model is constructed for response functions: alkaline pH number, oil color (OC) of mechanical impurities content (\( \beta \)). The research results showed that this coagulant improves the color of used oil. The use of this coagulant increases the alkaline number of purified oil. It reduces the content of mechanical impurities.

1. Introduction

Agricultural enterprises use a significant amount of motor oils to ensure the performance of both mobile (tractors, cars, combines) and stationary equipment. After the use of motor oils for their intended purpose in the oils are formed products of destruction of the oils themselves, as well as pollution resulting from the interaction of power plants with the environment and wear and tear of these installations. As a result of decay and imperfection of the collection system, after draining from the power plant in agricultural enterprises 80-85% of used motor oils (UMO) are formed, which do not meet the requirements of operation and represent a serious environmental problem, as they contain carcinogenic substances, heavy metals and toxic elements. In terms of component composition they contain additives and products of their decomposition (4-8%), low and high molecular acids, resins, carbens, carboids and other products of oil destruction (up to 3%), organic compounds of zinc, barium, calcium, sulfur, phosphorus (up to 2%), as well as carcinogenic incomplete combustion and products of engine parts wear. Uncompleted technology of UMO disposal leads to air, soil and water pollution.

Cleaning up UMO is a topical issue for agricultural enterprises. In recent years, agricultural enterprises use UMO purification directly in enterprises with subsequent use in those units and mechanisms that under operating conditions allow the use of such oils, which reduces the economic burden through the reuse of oils and reduce the environmental problem. The analysis shows that when oils are replaced, their physical and chemical properties practically do not change. Oils are contaminated with mechanical impurities and wear products of the oils themselves (acids, oxy acids, carbenes, carboids), which have a wide dispersed composition.
The process of UMO purification only by physical methods of purification (sedimentation, centrifugation, filtration) does not allow to obtain oils that meet modern requirements [1]. They are effective in removal of large particles with high density and less effective in removal of small particles with low density. Ultrafiltration is used to remove such particles, which has significant limitations due to high cost of filters and their low resource. The contamination of such filters occurs within 4-7 hours depending on the contamination of the UMO [2].

The efficiency of cleaning UMO from the smallest particles of impurities can be increased by coagulation (enlargement) of the smallest particles into conglomerates of large size and mass. Various types of coagulants are used for this purpose. To date, many issues associated with the use of coagulants to improve the efficiency of UMO treatment have not been resolved [3]. Therefore, studies in this area are of great interest and relevance.

The purpose of this work is to study the possibility of intensification of UMO purification process using organic or inorganic coagulants [4].

2. Materials and methods
The following studies have been carried out to achieve this objective:
- laboratory studies of physical and chemical properties of UMO;
- laboratory research into coagulant efficiency;
- comparison of characteristics of purified UMO and initial UMO;
- laboratory analysis of the content of wear products in oil by spectral method on the MPS-7 unit;
- potentiometric titration to determine the alkaline number of oils.

M10G2 was used as a UMO for testing. This is due to the fact that this oil takes a leading place in agricultural enterprises. In addition, it is highly alkaline and represents a serious problem at clearing, in view of soap formation.

Analysis of patent and literature sources showed that aqueous solutions of inorganic salts (sodium carbonate, trisodium phosphate), aqueous solutions of urea, thiocarbamide, methylethyl ketone and other substances are proposed to be used as coagulants [5].

In experimental studies, combinations of aqueous solution of urea, acetic acid and isopropyl alcohol were used as coagulants [6].

To evaluate the structure, three samples of coagulant were prepared and a series of experiments were conducted.

| No. | Coagulant Components | Coagulant options |
|-----|----------------------|-------------------|
|     |                      | I  | II | III |
| 1   | Acetic acid          | 20 | 40 | 40  |
| 2   | Carbamide            | 40 | 20 | 40  |
| 3   | Isopropyl alcohol    | 40 | 40 | 20  |

Effectiveness of coagulants was determined in 3 stages.

At the first stage, to eliminate the effect of water on the coagulant efficiency, the water in the UMO was removed by evaporation. Evaporation of water was carried out in parallel with cleaning the oil from large mechanical impurities [7]. The temperature during the deposition was maintained at the level of 100-105°C [8]. The water was evaporated in parallel with the oil from large mechanical impurities. The limiting process of sedimentation is the evaporation of water, as large particles are removed during centrifugation. To estimate the evaporation time of water, a series of experiments were carried out to determine the most efficient evaporation time [9, 10]. Varying factors were the moisture content of the oil in percentage, evaporation temperature t, °C and oil layer height during evaporation h, m.

As a result of experimental data processing, the regression dependence of the following type was obtained 1:

$$\tau = 10.346 + 18.34W - 0.0088t + 1.1h$$  (1)
Error of experimental data approximation was carried out according to the criterion of determination $R^2$ determined by the formula 2:

$$R^2 = 1 - \frac{\sum_{i=1}^{n}(Y_i - \hat{Y}_i)^2}{\left(\sum_{i=1}^{n}Y_i^2 - \frac{1}{n}\sum_{i=1}^{n}\bar{Y}_i^2\right)}$$

where $Y_i, \hat{Y}_i$ are function values in i-th experimental volume and calculated by approximation formula; $n$ is the number of experimental points.

The formula is fair in the range of parameter changes $0.1 \leq W \leq 0.5; 20 \leq t \leq 120^\circ C; 0.1 \leq h \leq 0.5m$.

Determination factor is $R^2 = 0.964$, which indicates a high correlation of the regression model with the experimental data. Calculations carried out according to formula (2) allowed determining the time of water evaporation in the waste oil by the actual water content. After draining removing mechanical impurities and solid products of oil destruction, the physical and chemical and operational parameters of sedimentary UMO were checked.

At the second stage the stationary oil was centrifuged at rotor speed $n = 6000 \text{ min}^{-1}$, oil temperature $70^\circ C$ during 20 min.

The oil obtained after centrifugation contains impurities not exceeding 5 - 7 µm, but the direct ultrafiltration of such oil is associated with rapid contamination of the ultrafilter, loss of pressure at the filter and reduced productivity of the filtration process.

In the third stage, the efficiency of the coagulant was directly determined using oil obtained in the second stage. The following parameters were considered when choosing the most effective coagulants for use in agricultural enterprises: distribution, cost, environmental safety.

Efficiency of coagulant was assessed in accordance with GOST 1770-74 and oil color was determined in accordance with GOST 20284-74 Petroleum products. Method for determination of color on colorimeter for determining the color of dark oil products (CDO).

The amount of coagulant was taken as being equal to 3%. Oil, preheated to 110-120°C, was poured into 100 ml beaker and a coagulant was added. After settling, the oil was filtered for 5 hours. White tape filter paper according to GOST 12026-76 was used.

The filtrate color was determined on the FEC-56M photo calorimeter. The mass of mechanical impurities was determined by drying the "white belt" filter with sediment at 75-80°C to a constant mass.

The characteristics of the variable factors are presented in Table 2.
Table 2. Characteristics of Variable Factors

| Factor               | Symbol | Factor value | Natural | Encoded |
|----------------------|--------|--------------|---------|---------|
| Coagulator Content   | \(\alpha\) | 0 1 2 -1 0 +1 |
| Retention temperature, °C | \(t\) | 60 100 -1 0 +1 |
| Drainage time, min.  | \(\tau\) | 10 20 30 -1 0 +1 |

3. Results and Discussion

The initial UMO selected from pallets of tractors had physical and chemical properties presented in Table 3.

Table 3. Physico-chemical properties of UMO, selected in farms of Omsk region

| Sample number | Physico-chemical properties of oils | \(v \cdot 10^6\) m²/s | \(t_{ign}, ^{\circ}C\) | \(\rho, \text{kg/m}^3\) | W, % | \(pH, \text{mg/g of oil Acid number}\) | Color, unit CDO |
|---------------|------------------------------------|-----------------------|----------------------|-----------------------|-------|------------------------------------------|----------------|
| 1             |                                    | 12.8                  | 175                  | 890                   | 0.25  | 2.08                                     | 0.10 8.2         |
| 2             |                                    | 13.6                  | 178                  | 902                   | 0.12  | 2.03                                     | 0.16 8.8         |
| 3             |                                    | 12.8                  | 181                  | 898                   | 0.01  | 3.15                                     | 0.14 8.7         |
| 4             |                                    | 11.0                  | 176                  | 893                   | 0.26  | 2.82                                     | 0.13 8.2         |
| 5             |                                    | 10.9                  | 177                  | 896                   | 0.08  | 3.16                                     | 0.08 8.0         |
| 6             |                                    | 13.5                  | 187                  | 904                   | 0.17  | 2.07                                     | 0.12 8.6         |
| 7             |                                    | 13.2                  | 188                  | 904                   | 0.02  | 3.34                                     | 0.12 8.6         |
| 8             |                                    | 11.8                  | 177                  | 891                   | 0.14  | 2.76                                     | 0.06 8.8         |
| 9             |                                    | 11.7                  | 177                  | 900                   | 0.22  | 2.71                                     | 0.11 8.9         |
| 10            |                                    | 12.4                  | 180                  | 903                   | 0.30  | 2.59                                     | 0.07 8.9         |
| 11            |                                    | 12.7                  | 181                  | 901                   | -     | 2.04                                     | 0.14 8.7         |
| 12            |                                    | 13.5                  | 190                  | 901                   | 0.23  | 2.24                                     | 0.15 8.7         |
| 13            |                                    | 11.1                  | 179                  | 896                   | -     | 1.92                                     | 0.12 8.5         |
| 14            |                                    | 11.6                  | 180                  | 899                   | 0.01  | 2.21                                     | 0.05 8.8         |
| 15            |                                    | 11.8                  | 180                  | 903                   | 0.15  | 2.33                                     | 0.11 8.9         |
| 16            |                                    | 13.6                  | 188                  | 901                   | -     | 2.57                                     | 0.08 8.4         |
| 17            |                                    | 12.4                  | 180                  | 900                   | 0.30  | 3.28                                     | 0.08 8.3         |
| 18            |                                    | 11.6                  | 177                  | 978                   | 0.19  | 3.66                                     | 0.05 8.7         |
| 19            |                                    | 11.7                  | 173                  | 988                   | 0.17  | 3.25                                     | 0.09 8.6         |
| 20            |                                    | 11.7                  | 175                  | 987                   | -     | 3.77                                     | 0.04 8.7         |
| Average       |                                    | 12.07                 | 179.95               | 911.75                | 0.131 | 2.704                                    | 0.101 8.6        |
| Lower deviation|                                  | 1.17                  | 4.95                 | 21.75                 | 0.121 | 0.784                                    | 0.061 0.4        |
| Upper deviation|                                  | 1.53                  | 10.05                | 76.25                 | 0.129 | 1.066                                    | 0.059 0.3        |

The analysis of Table 3 shows that physical and chemical properties of UMO in their composition slightly differ from each other. The average kinematic viscosity at 100°C is 12.07 mm²/s. The minimum deviation is 1.17 mm²/s, and the maximum deviation is 1.53 mm²/s. The flash point has an average value...
of 179.95 with a minimum deflection of 4.95 °C and a maximum deflection of 10.05 °C. The oil color was between 8.2 and 8.9 CDO with an average value of 8.6.

The analysis of the given oil samples shows that barium content did not exceed 0.1% and calcium content was less than 0.06%. Maximum PH value was equal to 3.77 mgCon/g. oils. The lower viscosity and flash point values indicate that the UMO fuel was contaminated.

Research of coagulants efficiency used the mixture of UMO physical and chemical properties presented in Table 4. The mixture was prepared by mixing of different oil samples.

**Table 4.** Physico-chemical properties of UMO mixture used for coagulant efficiency estimation.

| Sample number | ν·10⁶, m²/s | tigs, °C | ρ, kg/m³ | W, % | pH, mg/g of oil | Acid number | Color, unit CDO |
|---------------|-------------|---------|----------|------|----------------|-------------|---------------|
| 1             | 12.1        | 176     | 890      | 0.08 | 2.08           | 0.10        | 8.6           |

The results of laboratory experimental determination of coagulant variant are presented in Table 5.

**Table 5.** Evaluation of efficiency of coagulant variants

| Coagulant variant | pH, mgCon/g of oil | Color, unit CDO | Mechanical impurities, % |
|-------------------|-------------------|----------------|-------------------------|
| I                 | 3.24              | 7.5            | 0.022                   |
| II                | 2.96              | 7              | 0.019                   |
| III               | 2.88              | 6.5            | 0.016                   |

Analysis of Table 5 data shows that the third variant of coagulant is the most effective (Table 1). The results of subsequent laboratory studies are presented for this coagulant variant.

As a result of experimental data processing, mathematical models were obtained:

\[
pH = 2.07 + 0.00003232\alpha + 0.000286\tau + 0.000277 + 0.00006052\alpha \cdot \tau + 0.0384\alpha \cdot \beta + 0.0000623\cdot \alpha \cdot \beta + 0.00000013\alpha^2 - 0.0000046\tau^2 - 0.00073
\]

Calculations of the influence of factors on alkaline number changes are shown in Figures 1-3.
Figure 3. Change in the alkaline number of UMO as a function of temperature $t \, ^{\circ}C$ and residence time $\tau \, \text{min}^{-1}$ at coagulant percentage $\alpha=1 \%$

From the analysis of the diagrams presented in Figures 1-3, we can see that an increase in the percentage of coagulant leads to an increase in the alkaline number. The alkaline number increases in the same way as temperature and settling time increase. Depending on the settling temperature, the surface has an inflection line corresponding to the temperature of 70°C. At temperatures between 60 and 70 °C, the alkaline number increases intensively, and after 70 °C the growth rate slows down.

Depending on the settling time, the surface has a knick line corresponding to the settling time of 15 minutes. At the resting time in the range from 0 to 15 minutes there is an intensive growth of pH, and in the range from 15 to 30 minutes the growth of pH slows down.

As a result of experimental data processing, a mathematical model reflecting the influence of coagulation factors on oil color 5 was obtained:

$$CO = 9 - 0.007\alpha - 0.011946t - 0.00243\beta - 0.00152\alpha^2 - 0.0000452t^2 - 0.0000484\beta^2$$  (5)

Calculations carried out according to formula 2 allowed to plot the dependence of oil color on these factors:

Figure 4. Change of color of UMO depending on percentage of coagulant $\alpha \, (\%)$ and temperature of sediment $t \, (^{\circ}C)$ at the duration of sedimentation of 20 min.; temperature of sediment: 1 - 60 °C, 2 - 70 °C, 3 - 80 °C, 4 - 90 °C, 5 - 100 °C.

Figure 5. Dependence of oil color on coagulant content $\alpha(\%)$ and retention time $\tau \, \text{(min)}$ at retention temperature $t=80 \, ^{\circ}C$. 
Analysis of the graphs in Figures 4-6 shows that the coagulant percentage, temperature and residence time improve the oil color, which confirms the removal of the smallest particles of organic and inorganic contaminants from the oil during coagulation and residence.

To reflect the change in the content of mechanical impurities in oil during the coagulation process, a mathematical model of the following type has been obtained:

\[
Y = 0.0746 - 0.00063\alpha - 0.00004736t - 0.0000367\beta - 0.0000126\alpha^2 - 0.00000446t^2 - 0.000034\beta^2
\]

To illustrate the influence of factors on the removal of mechanical impurities from the oil, diagrams of \(\gamma\) change, shown in Figures 7-9, are calculated.

**Figure 6.** Dependence of oil color on temperature \(t\) (°C) and residence time \(\tau\) (min) at coagulant percentage \(\alpha=1\%\)

**Figure 7.** Change in the content of mechanical impurities as a function of the percentage of the coagulare \(\alpha\) (%) and the temperature of sedimentation \(t\) (°C) at the sedimentation time of 20 min.

**Figure 8.** Changes in the content of mechanical impurities as a function of the percentage of coagulant \(\alpha\) (%) and residence time \(\tau\) (min) at residence temperature \(t=80\,^\circ\)C.
The analysis of coagulant influence on change of the content of mechanical impurities in oil shows that at increase in the coagulant content, time, and temperature of the sedimentation, the content of mechanical impurities in the process of sediment decreases. The content of mechanical impurities at 1% coagulant, 30 minutes of a sedimentation at a temperature of 80 °C has decreased from 0.07 % to 0.033% and at a temperature of 100 °C – to 0.017 %.

4. Conclusion
The results of a studying the coagulant consisting of 40% acetic acid, 40% urea and 20% isopropyl alcohol showed:

1. The coagulant effectively improves the color of used oil from 8- 9 CDO to 6 – 6.5 CDO.

2. The use of coagulant for UMO purification slightly increases the alkaline number of purified oil. Depending on the treatment mode, the pH increase is 10-15%.

3. The content of mechanical impurities at 1% coagulant, 30 minutes of exposure at 80 °C decreased from 0.07% to 0.033%, and at 100°C it decreased to 0.017%.

4. The proposed coagulant composition can be used for pre-treatment of UMO under ultrafiltration.

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