ELECTRIFICATION OF PETROLEUM FUELS

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Petroleum fuels (gasolines, kerosenes, diesel fuels, etc.) are dielectrics. During the operations of decantation, pouring, and pumping through large pipelines and hoses, they are electrified. The accumulation of electrostatic charges in the volume of a fuel in reservoirs, different vessels, and equipment constitutes a serious danger in industrial processes. Cases of the ignition and explosion of petroleum fuels resulting from discharges of static electricity are known in practice.

In recent years, there has been increased interest in the electrification of petroleum products. However, the accumulation of experimental data is still insufficient, and there is no complete concept with respect to this phenomenon.

THEORETICAL CONSIDERATIONS

The electrification of petroleum fuels is due to the presence of certain types of impurities, mainly electrolytes whose molecules in a hydrocarbon medium are capable of dissociating into ions. The mechanism of electrification comes down to the fact that ions of the same sign existing in a liquid are adsorbed on the surface of a solid (the wall of a tube), while ions of the opposite sign are distributed in the volume of the liquid. With movement of the liquid, the electric charges distributed in its volume are entrained by the flow and, together with the liquid, accumulate in the receiving reservoir. The adsorbed charges on the wall of the tube are freed, and if the tube is metallic and grounded, are neutralized.

Kosman and Gavis [1] proposed a theory of the formation of charges in liquid dielectrics with their turbulent flow through tubes; the theory is based on the transfer of ionic charges by diffusion, conductivity, and convection. According to the theory, the value of the current force. i, of the electrification of the flow of a liquid in a pipeline with radius a and length L is determined from the equation:

$$i = \pm \frac{\pi \varepsilon \varepsilon_0 R T v}{2NF} \mathrm{Nu} \left(1 - \frac{n}{n_0}\right)\left[1 - \exp\left(-\frac{L}{v\tau}\right)\right], \tag{1}$$

where ε and ε_0 are the dielectric permeabilities of the liquid and of a vacuum, respectively; R is the universal gas constant; T is the absolute temperature of the liquid; v is the mean rate of movement of the liquid; N is the transfer number of ions of opposite sign; F is the Faraday number; Nu is the Nusselt number; n_0 and n_W are, respectively, the concentrations of ions in the volume of the liquid and on the surface of the tube wall; τ is the relaxation time of the liquid.

It is assumed in Eq. (1) that the specific conductivity of the liquid, γ, is equal to:

$$\gamma = \frac{2n_0 D_M F^2}{RT}, \tag{2}$$

while the effective thickness of the diffusion layer, d, that is, the thickness of the layer of liquid near the wall, closely bound to the surface, is equal to:

$$d = \frac{2a}{\mathrm{Nu}}, \tag{3}$$

where D_M is the coefficient of molecular diffusion.

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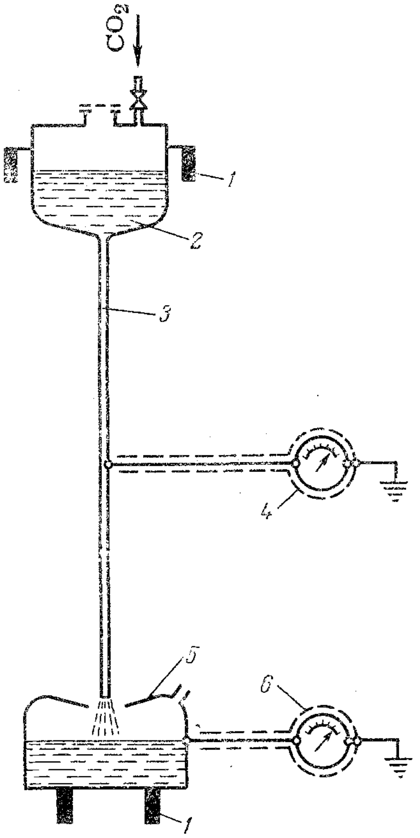

Fig. 1. Schematic diagram of unit for investigation of the electrification of petroleum fuels in a flow: 1) fluoroplastic insulators; 2) supply reservoir; 3) stainless steel tube with diameter of 4 mm; 4) direct current electrometric amplifier; 5) receiving reservoir; 6) electrostatic voltmeter.

From the relationships describing mass transfer in turbulent flow it follows that the diffusion of ions to the wall of the tube obeys the laws for the transfer of mass or heat at high Schmidt or Prandtl numbers. Here no account is taken of such factors as the valence of the electrolyte in a solution of the liquid and the roughness and the state of the inner walls of the tube, which have an effect on the value of the electrification current force.

In the derivation of Eq. (1) it was postulated that ions of only one valence are present in the liquid. It is well known, however, that the electrification of liquid hydrocarbons depends on the presence in them of such dissociated impurities as heteroorganic compounds with high polarity, as well as solid colloidal particles. In light petroleum products, for example, jet fuels, with long-term storage and pumping, there can accumulate so-called microimpurities due both to the corrosion products of the metals and the surrounding dust and to processes involving the oxidation of the unstable components of the petroleum products. Consequently, the transfer of charges in liquid hydrocarbons may involve the participation both of ions of different valence (monovalent, divalent, multivalent ions), and of relatively large colloidal particles, and the actual value of the electrification current force of the flow can be considerably greater than that calculated using formula (1).

The effect of the above-listed factors on the value of the current strength of the electrification of the liquid flow may be taken into account using the coefficient K which, in turn, consists of the following two coefficients:

$$K = \alpha_1 \alpha_2,$$

where α_1 is a coefficient depending on the character of the ions in the liquid (mono- and polyvalent or groups of ions); α_2 is a coefficient characterizing the roughness of the internal walls of the tube and their state [1, 5].

The value of these coefficients must be determined experimentally.

Using the coefficient K and the relationship for the Nusselt number $\mathrm{Nu} = 0.0223\,\mathrm{Re}^{7/8}\mathrm{Sc}^{1/4}$, where $\mathrm{Sc} = \nu / D_M$ is the Schmidt number and ν is the kinematic viscosity of the liquid, Eq. (1) is transformed to the following form which is convenient for practical calculations:

$$i = \pm K \frac{0{,}035 \varepsilon\varepsilon_0 R T v}{NF} \mathrm{Re}^{7/8}\, \mathrm{Sc}^{1/4} \left(1 - \frac{n_c}{n_0}\right) \left[1 - \exp\left(-\frac{L}{v\tau}\right)\right]. \tag{4}$$

It can be assumed that the current strength for the electrification of petroleum fuels in pipelines depends on the following factors: the dielectric properties and the kinematic viscosity of the liquid; the flow rate; the dimensions of the pipeline and its length; the material of the pipeline; the roughness and the state of its inner walls; the temperature of the liquid.

EXPERIMENTAL INVESTIGATIONS

Experimental investigations of the electrification of petroleum fuels in a flow were carried out in the laboratory of the I. M. Gubkin Moscow Institute of the Petrochemical and Gas Industry in two different units, I and II, consisting of supply and receiving reservoirs and a pipeline in which the flow of the fuel was established.

In unit I (Fig. 1) the fuel was poured from the supply reservoir into the receiver (both with a capacity of 10 liters) through a vertically arranged tube made of stainless steel, with a diameter of 4 mm, under the pressure of the column of liquid or of gas. Both reservoirs were insulated from the ground and from each other using special insulators made of Fluoroplastic-4. The resistance of an insulator exceeded 10^{13} Ω. The pouring tubes could be varied by increasing the column of liquid or by setting up an excess gas pressure in the supply reservoir. During the time of a single experiment the flow rate in the tube was constant within the limits of about 1%.

TABLE 1. Properties of Petroleum Products Investigated

Petroleum product	Density, ρ_4^{20}	Viscosity at 20°C, cS	Specific volumetric electrical resistance, ρ_V, $\Omega \cdot$ m	Dielectric permeability, ε
B-70 gasoline	742	1.16	$2.54 \cdot 10^{11}$	1.99
B-70 gasoline	742	1.16	$2.20 \cdot 10^{11}$	1.99
Illuminating kerosene	785	1.53	$9.60 \cdot 10^{10}$	2.08
T-1 jet fuel	800	1.53	$6.78 \cdot 10^{10}$	2.10
T-1 jet fuel	800	1.53	$5.35 \cdot 10^{10}$	2.10
T-1 jet fuel	807	1.64	$1.67 \cdot 10^{10}$	2.11
B-70 gasoline with addition of magnesium oleate in a concentration of 0.001 g/liter	742	1.16	$3.10 \cdot 10^{10}$	2.01
Diesel fuel	883	3.76	$1.86 \cdot 10^{10}$	2.23
B-70 gasoline with addition of magnesium oleate in a concentration of 0.01 g/liter	742	1.16	$8.50 \cdot 10^{9}$	2.00
Gas oil	881	5.48	$5.88 \cdot 10^{9}$	2.32
B-70 gasoline with addition of chromium naphthenate in a concentration of 0.1 g/liter	742	1.16	$3.00 \cdot 10^{9}$	1.98
Crude oil	855	12.33	$6.50 \cdot 10^{7}$	2.24

TABLE 2. Results of Tests in Unit I with the Pouring of Crude Oil and Petroleum Products

Petroleum products	Rate		Reynolds number, Re	Current force of electrification of flow, i, A $\cdot 10^{10}$	Density of charges of flows, ρ μC/m^3
	of pouring, q, cm^3/sec	of flow in pipeline, v, m/sec			
B-70 gasoline ($\gamma = 3.94 \cdot 10^{-12}$ $\Omega^{-1} \cdot m^{-1}$)	16.7	1.33	4590	14.00	84.0
B-70 gasoline ($\gamma = 4.55 \cdot 10^{-12}$ $\Omega^{-1} \cdot m^{-1}$)	16.7	1.33	4590	11.50	69.0
Illuminating kerosene	15.4	1.23	3220	7.10	46.0
T-1 jet fuel ($\gamma = 1.48 \cdot 10^{-11}$ $\Omega^{-1} \cdot m^{-1}$)	15.4	1.23	3200	5.00	32.4
B-70 gasoline with addition of magnesium oleate with a concentration of 0.001 g/liter	18.2	1.45	5000	3.30	18.1
Diesel fuel	14.3	1.14	1215	0.77	5.4
B-70 gasoline with addition of magnesium oleate with a concentration of 0.01 g/liter	18.2	1.45	5000	0.60	3.3
Gas oil	10.5	0.84	615	0.29	2.8
B-70 gasoline with addition of chromium naphthenate with a concentration of 0.1 g/liter	16.7	1.33	4590	0.40	2.4
Crude oil	6.1	0.49	159	0.15	2.5

In unit II, the fuel was pumped under gas pressure from the supply reservoir into the receiver (both with a capacity of 200 liters) through stainless steel pipelines of different diameters and different lengths. The unit was insulated from the ground by cylindrical insulators made of Fluoroplastic-4, while the pipeline was insulated from the reservoirs using insulating flanges made of the same material. The resistance of the insulation exceeded $10^{13}\,\Omega$.

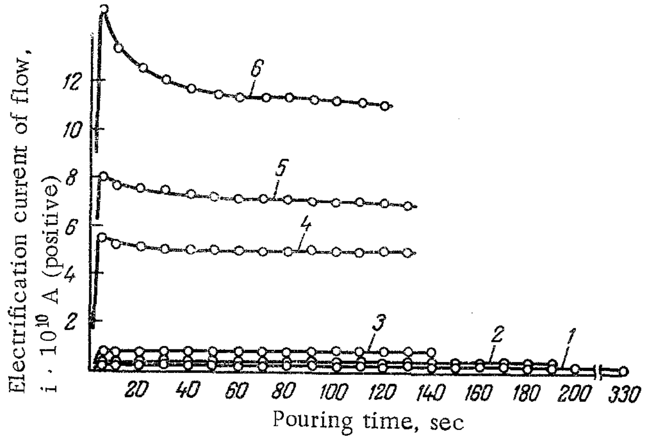

Fig. 2. Dependence of the electrification current on the pouring time for unit I. Two liters of petroleum products: 1) crude oil; 2) gas oil; 3) diesel fuel; 4) T-1 fuel; 5) illuminating kerosene; 6) B-70 gasoline.

Experimental investigations were carried out using pipelines with inside diameters of 4, 6, 8, 10, 13, and 16 mm, and lengths from 1 to 8, 19 mm. The supply reservoir of the unit was designed for a pressure of 15 atm, and the pumping rate could be varied over wide limits from 0.1 to 7 m^3/h and over.

The electrification investigations were carried out using crude oil and various types of fuel: gas oil, diesel fuel, three different portions of T-1 jet fuel, illuminating kerosene, two different portions of B-70 gasoline, and B-70 gasoline with different antistatic additives in different concentrations. Laboratory analysis of the quality of the petroleum products was carried out according to GOST (All-Union State Standard) 3900-47 and GOST 33-53, while their dielectric properties were determined according to GOST 6581-53 on liquid dielectrics. The unit for determining the specific volumetric resistance used flat electrodes, cylindrical electrodes were used for measuring the dielectric permeability. Table 1 gives the mean values of the quality indices and the dielectric properties of the crude oil and the petroleum products obtained from three samples at a temperature of plus 20°C. As a rule, the specific resistance was measured before and after the experiments. It is very evident that the dielectric permeability of both the crude oil and the different types of petroleum products differs only slightly and can be assumed equal to two. The specific volumetric resistance is very different. For light petroleum products it is 1000-10,000 times higher than for crude.

The electrification of petroleum fuels in a flow was determined from the magnitude and the direction of the currents flowing between the pipelines being tested and the ground. The currents were measured using magnetoelectric galvanometers with a type M 195/3 luminous dial and a scale division of $1.5 \cdot 10^{-9}$ A, and a dc Type VI-2 electrometric amplifier with a measurement range of from $1 \cdot 10^{-13}$ to $0.5 \cdot 10^{-6}$ A. The error in measurement of the current force was not more than ±5%. The measuring instruments were connected to the current source using a shielded cable. To ensure the best shielding from stray currents, both the shield of the cable and a special shield for the instrument itself were connected to the terminal of the "ground" of the instruments.

The experiments were made in the following manner. The supply reservoir of the unit and the pipeline were filled with the fuel to be investigated, in amounts from 2 to 200 liters. Then, under the pressure of the column of liquid or of the gas, the fuel was pumped at a constant rate through the pipeline into the receiving reservoir. At first every 2-5 sec (depending on the pumping rate), and then every 10 sec, measurements were made of the strength and direction of the current between the pipeline and the ground and of the mean pumping rate of the fuel. The current strength was measured with instruments connected between the supply and receiving reservoirs, or only the receiving reservoir (in unit I) and the ground.

As a result of the experiments, the following laws were established governing the electrification of flows of petroleum products.

Effect of Pumping Time. Figure 2 shows the dependences of the mean values of the current forces for the electrification of the flow on the pouring time of 2 liters of crude and petroleum products through a stainless steel pipeline measuring 6 × 1 mm, with a length of 2 m, under the pressure of the column of liquid. The data were obtained at the following pouring temperatures, °C: crude-25; gasoline, diesel; and jet fuels-23; kerosene-23.5; gaso-

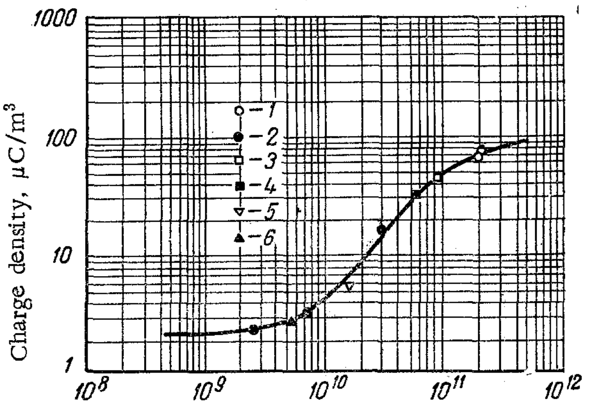

Fig. 3

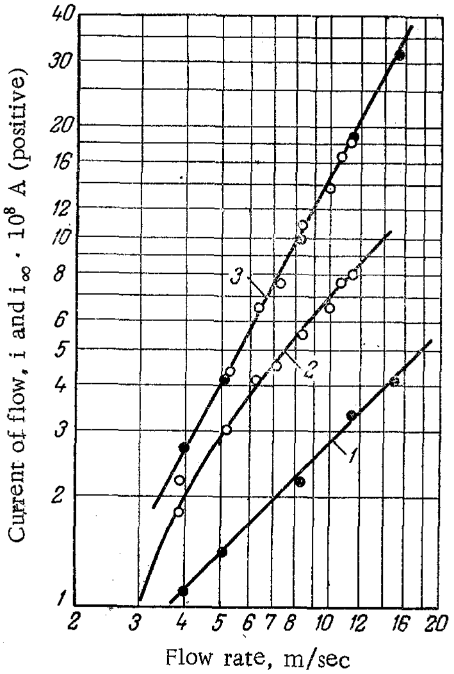

Fig. 4

Fig. 3. Dependence of electrification of petroleum products on their specific volumetric resistance (flow rate 0.84-1.45 m/sec; pipeline made of stainless steel, with a diameter of 4 mm and a length of 2 m): 1) B-70 gasoline; 2) B-70 gasoline with antistatic additives; 3) illuminating kerosene; 4) T-1 jet fuel; 5) diesel fuel; 6) gas oil.

Fig. 4. Dependence of the electrification current on the flow rate of T-1 jet fuel at a temperature of 18.5-23°C.

line-24. Three experiments were made with each sort of petroleum product; the results of the experiments differed only slightly.

It became apparent that, when poured through a steel pipeline, crude oil and petroleum products take on positive charges. Simultaneously, free negative charges appear on the surface of the pipeline. The positive charges accumulate in the petroleum products of the receiving reservoir. The reservoir takes on a potential difference with respect to the ground, which increases with the pouring of the petroleum products. The potential difference was measured with an electrostatic voltmeter, connected between the reservoir and the ground.

It was found in the experiments that a greater number of charges is formed per unit time during the initial pouring period than in the following period with fully established pouring conditions. It is found in Fig. 2 that, under given pouring conditions, the time required for the establishment of steady-state conditions is from 10 sec for diesel fuel up to 40 sec for B-70 gasoline. The experimentally determined values of the electrification current force for gasoline exceed by almost 50% the mean values of the current force determined with the subsequent establishment of steady-state electrification conditions. For other sorts of petroleum products this difference in the current force is considerably less.

In tests of the pumping of T-1 jet fuel under gas pressure in unit II, through pipelines made of stainless steel of different dimensions and lengths at different rates, a dependence was established of the force of the electrification current of the flow on the pumping time analogous to that for B-70 gasoline. However, the time required for establishment of steady-state conditions for T-1 is from 20 sec up to 1 min depending on the pumping rate.

The laws found governing the strengthening of the electrification of the flow of the fuels during the initial pumping period can be explained by the rate of formation of a double electric layer at the solid-liquid interface. The process of the diffusion of the ions in the liquid toward the wall of the pipeline takes place in time and arises when the liquid is already in contact with the surface of the tube, that is, before the start of pumping.

Effect of Dielectric Properties. Table 2 gives mean pouring rates and rates of flow in the pipeline, mean values of the electrification current force, and of the charge density under fully established conditions, obtained in unit I with the pouring of crude and of various petroleum products through a pipeline of dimensions 6 × 1 mm and a length of 2 m, under the pressure of the column of liquid. The measured values of the potential difference of the receiving reservoir and the values calculated from its charge density are not given, since the latter differ only slightly from the densities given in Table 2, calculated from the mean values of the current force.

It is evident from Fig. 2 that, under the given conditions (flow rate of all sorts of products varied over wide limits, from 0.84 to 1.45 m/sec) light petroleum products are electrified considerably more strongly than dark petroleum products (with the exception of gasoline with antistatic addivites). In the presence of additives, the conductivity of the petroleum products is increased, as a result of which there is an increase in the loss of charges in their flow, and the electrification is decreased.

It is characteristic for all the sorts of petroleum products investigated that with an increase in their dielectric indices,(mainly, of the specific volumetric resistance) there is an increase in the density of the charges formed. The dependence of the volumetric charge density of a flow of petroleum products on their specific volumetric resistance, shown in Fig. 3 on a logarithmic scale, shows that, within certain limits of change in the specific resistance (for example, from $5 \cdot 10^9$ to $2 \cdot 10^{11}$ $\Omega \cdot$ m), the logarithm of the value of the charge density of the flow depends linearly on the logarithm of the mean specific resistance of the petroleum products. The slope of the curves is close to unity. Consequently, under the conditions of our experiments (variation of the flow rate from 0.84 to 1.45 m/sec) the volumetric charge density of the flow of petroleum products is approximately proportional to their specific volumetric resistance to the first power (up to definite limits).

The relationship obtained for the strengthening of the electrification with an increase in the specific resistance of petroleum products up to a value on the order of 10^{11} $\Omega \cdot$ m has been observed in laboratory work [2]. In [1] the same relationship is given up to a value of the specific resistance of approximately $5 \cdot 10^{11}$ $\Omega \cdot$ m at a flow rate of 1.5 m/sec. With an increase of the flow rates this limit shifts toward the side of lower specific resistances ($5 \cdot 10^{10}$ $\Omega \cdot$ m).

Effect of Flow Rate. Figure 4 gives the dependence of values of the force of the electrification current on the flow rate for two different portions of T-1 jet fuel, obtained in unit II with a stainless steel pipeline measuring 6 × 1 mm and a length of 2 m, with a conductivity of the fuel, $\Omega^{-1} \cdot m^{-1}$: 1) $1.87 \cdot 10^{-11}$ and 2) $6 \cdot 10^{-11}$. Curve 3 reflects values of the force of the electrification current, calculated for a tube of infinite length: the open points refer to a fuel with a conductivity of $6 \cdot 10^{-11}$ and the black points to a fuel with a conductivity of $1.87 \cdot 10^{-11}$ $\Omega^{-1} \cdot m^{-1}$.

Curve 3, Fig. 4, was plotted from values of the current force, obtained using the formula:

$$i_{\infty} = \frac{i}{1 - \exp(-L/v\tau)}, \tag{5}$$

where i are values of the current force measured in experiments with L = 2 m. All the points, where the parameter $L/v\tau < 1$, lie on a single straight line with a slope of about 1.875. The same result was obtained in experiments with pipelines of other sizes and lengths. Consequently, the current force i_{∞} is proportional to the flow rate of the fuel to the 1.875 power.

Effect of Diameter and Length of Pipeline. To establish the effect of the diameter of the pipeline, a curve was plotted of the dependence of the value of $\log(i_{\infty}/v^{1.875})$ on the logarithm of the diameter of the pipeline for all the tube sizes tested. It was found that the current strength for electrification of the flow of fuel is proportional to the diameter of the pipeline to the 0.875 power.

To establish the effect of the length of the pipeline, a curve was plotted of the dependence of the value of $i/(2a)^{0.875}$ on the parameter $[1-\exp(-L/v\tau)]$ for tubes of different lengths, from 1 to 8 m. It was found that the dependence of the current force for electrification of the current on the length of the pipeline is represented in the form $i \sim [1-\exp(-L/v\tau)]$.

Value of the Coefficient K. For the flow of all the fuels investigated in pipelines of all sizes and lengths tested, a curve was plotted of the dependence of the value of $\log[i_{\infty}/(2a)^{0.875} \times v^{1.875}]$ on the logarithm of the parameter $G = 4a^2/Re^{1.75}\tau\nu$. All the experimental data lie closely along a single curve. The experimental data of other authors [3-6] for the flow of various petroleum products, analyzed by the above method, also lie close to the curve obtained for the electrification of petroleum fuels.

According to the experimental data for the flow of petroleum fuels, the coefficient K was found equal to 10: this value must also be used in calculations using formula (4).

CONCLUSIONS

1. The volumetric charge density in the flow of a fuel, within certain limits, is linearly dependent on its specific volumetric resistance.

These limits vary depending on the flow rate.

2. For a fuel with a low conductivity, the current force for the electrification of a turbulent flow in a pipeline of great (more precisely, infinite) length is proportional to the flow rate to the 1.875 power.

3. The current force for the electrification of the turbulent flow of a fuel is proportional to the diameter of the pipeline to the 0.875 power. With an increase in the length of the pipeline, within known limits, it increases.

4. The theory of Kosman and Gavis [1] describes correctly the process of the electrification of petroleum products with their turbulent flow in pipelines; however, it does not take account of various charge carriers in industrial petroleum products, as a result of which it yields too low a value of the current strength for the electrification of the flow of petroleum fuels.

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