# PHYSICS

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1968

SovietRxiv

## Abstract

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# ON FLASH HETEROPHASE LUMINESCENCE IN ORGANIC LIQUIDS UNDER THE ACTION OF STRONG ELECTRIC FIELDS

*(Presented by Academician V. N. Kondrat' ev, 10 VII 1967)*

**1.** It has recently been discovered that the electroluminescence of organic liquid dielectrics in steady electric fields ($^{1-4}$) contains, as one of its principal components ($^{5}$), light pulses randomly distributed in time ($^{5-8}$). These pulses, referred to below as electroflashes ($^{5}$), were observed in aromatic solutions of the liquid-scintillator (LS) type ($^{5,6}$), in transformer oil and liquid paraffin ($^{7}$), in hexane and heptane ($^{8}$), and also in many other liquids ($^{5,6}$). Electroflashes are associated with prebreakdown currents ($^{7}$), and there is even, apparently, a temporal correlation of these flashes with conduction-current pulses ($^{6}$).

The causes of the appearance of electroflashes were not clarified in ($^{6,7}$). According to ($^{1-4}$), electroluminescence of liquid dielectrics occurs as a result of direct excitation of liquid molecules by electrons emitted by the cathode. But for a number of reasons, one of which is discussed below, such a mechanism can hardly lead to the appearance of electroflashes. As will be shown in another paper, the explanation proposed by the authors of ($^{8}$), in which electroflashes are due to the action of dust particles suspended in the liquid, also raises objections.

In the present work attention is drawn to the similarity of electroflashes to flashes of sonoluminescence that arise when gaseous cavitation cavities collapse in liquids under the action of ultrasound. Data are presented below in support of the view that electroflashes arise not in the liquid phase, but in gaseous microcavities formed near the electrodes.

**2.** To study the flash electroluminescence of liquids, sealed cuvettes were used with flat parallel electrodes or with Rogowski electrodes ($^{9}$) made of stainless steel and finished with optical precision. The fixed interelectrode spacing was $h = 4$ mm. The interelectrode volume of liquid was viewed from a distance of 15 cm through a light guide by an FEU-13 photomultiplier; the signals from its output were investigated with an AI-100-1 multichannel analyzer and other electronic apparatus.

The liquids under study were dried over metallic sodium and poured into care-

Fig. 1. Effect of $\gamma$-rays of $Co^{60}$ on the amplitude spectrum of electric flashes in a standard LS based on toluene. 1—edge of the amplitude spectrum of $Co^{60}$ in the absence of an electric field; 2—spectrum of electric flashes at $V = 20$ kV without a $Co^{60}$ source; 3—spectrum of electric flashes at the same voltage in the presence of a $Co^{60}$ source with an activity of 0.5 mg-eq Ra at a distance of 4 cm from the center of the cuvette. Rogowski electrodes, $h = 4$ mm.

Figure 1: Fig. 1. Effect of $\gamma$-rays of $Co^{60}$ on the amplitude spectrum of electric flashes in a standard LS based on toluene. 1—edge of the amplitude spectrum of $Co^{60}$ in the absence of an electric field; 2—spectrum of electric flashes at $V = 20$ kV without a $Co^{60}$ source; 3—spectrum of electric flashes at the same voltage in the presence of a $Co^{60}$ source with an activity of 0.5 mg-eq Ra at a distance of 4 cm from the center of the cuvette. Rogowski electrodes, $h = 4$ mm.

fully washed cuvettes through No. 4 glass filters. In a number of experiments the liquids in the cuvettes were saturated with various gases. The experiments were carried out at atmospheric pressure and a temperature of about 20°C.

**3.** At a voltage on the electrodes of $V = 20$ kV, electroflashes were observed in $n$-heptane, $n$-octane, $n$-decane, benzene, toluene, xylenes, phenylcyclohexane, 1-methylnaphthalene, decalin, chloroform, carbon tetrachloride, chlorobenzene, perfluorobenzene, 1-bromonaphthalene, acetone, and also in paraffin and silicone oils. No organic liquid dielectric was found in which electroflashes did not appea-

would be observed. The results obtained are consistent with the data of (6) on the appearance of electric flashes not only in aromatic hydrocarbons but also in such nonluminescent liquids as ethylene glycol, methanol, acetone, and carbon tetrachloride.

The average threshold field strengths $\langle E\rangle_{\mathrm{th}} = V_{\mathrm{th}}/h$, at which flashes began to appear, were $10 \div 50$ kV/cm. The amplitudes of the electric flashes $A_{\mathrm{e}}$ in pure liquids were comparable with the amplitudes $A_{\mathrm{c}}$ of scintillations from $\gamma$-rays of $Co^{60}$ in the LS. The generation rates $\dot{N}$ of electric flashes above the noise level of the PMT at $V = 20$ kV and for the given experimental geometry varied, for different liquids, from $\sim 10^2$ flashes/min (pure hydrocarbons) to $\sim 10^5$ flashes/min (acetone). The largest values $A_{\mathrm{e}} > 10A_{\mathrm{c}}$ were shown by 1-methylnaphthalene and chlorobenzene, whereas for pure hydrocarbons $A_{\mathrm{e}} \lesssim A_{\mathrm{c}}$. Dissolution in pure liquids of fluorescent compounds of the type of activators and spectrum shifters for LS (PPP, PPO, POPOP) (10) led to an increase in $A_{\mathrm{e}}$. Unexpectedly, an increase in $A_{\mathrm{e}}$ and $\dot{N}$ was found as a result of adding to LS or aromatic liquids small amounts ($\sim 0.01\,M$) of such typical quenchers of luminescence in organic liquids and solutions as carbon tetrachloride, acetone, and acetic acid.

**Fig. 1.** Effect of $\gamma$-rays of $Co^{60}$ on the amplitude spectrum of electric flashes

Figure 2: graph

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in a standard LS based on toluene. 1—edge of the amplitude spectrum of $\mathrm{Co}^{60}$ in the absence of an electric field; 2—spectrum of electric flashes at $V = 20$ kV without a $\mathrm{Co}^{60}$ source; 3—spectrum of electric flashes at the same voltage in the presence of a $\mathrm{Co}^{60}$ source with an activity of 0.5 mg-eq Ra at a distance of 4 cm from the center of the cuvette. Rogowski electrodes, $h = 4$ mm.

During the measurements, considerable fluctuations of the quantities $\dot{N}$ and $A_{\mathrm{e}}$ were observed, similar to those described in (7). In addition, after the voltage was switched on, within several minutes a decrease of $A_{\mathrm{e}}$ and $\dot{N}$ to certain steady values was noted. After the cuvette had been operated for $\sim 100$ h, a noticeable irreversible decrease in $A_{\mathrm{e}}$ and $\dot{N}$ was observed.

4. Electric flashes were studied in detail in a standard LS, consisting of a solution of 4 g/l PPO and 0.1 g/l POPOP in toluene. For the given experimental geometry the threshold voltage $V_{\mathrm{th}}$ for this LS was $\sim 10$ kV. A further increase in the voltage led to an approximately exponential increase in $\dot{N}$, while the value of $A_{\mathrm{e}}$ increased sublinearly. As shown by comparison of $A_{\mathrm{e}}$ and $A_{\mathrm{c}}$ (taking into account the close similarity of the electroluminescence and radioluminescence spectra of the LS found in (6)), in one electric flash of maximum amplitude (Fig. 1), lasting $\sim 10^{-7}$ s, the LS emits $\sim 5 \cdot 10^{-4} \div 10^{5}$ photons of mean energy $h\nu \approx 3$ eV. A noticeable increase in $A_{\mathrm{e}}$ and $\dot{N}$ under the action of $\gamma$-rays of $\mathrm{Co}^{60}$ was found (Fig. 1).

The influence of saturating gases on electric flashes was studied in a standard LS based on toluene and in analogous LS based on 1-methylnaphthalene or xylene, as well as in pure aromatic solvents. As a result it was found that carbon dioxide, oxygen, and especially hydrogen quench electric flashes, whereas heavy noble gases (Ar, Xe) in-

cause an increase in the amplitudes and generation rates of electric flashes in aromatic liquids and solutions (Fig. 2). Some measurement results, characterized by the quantities $\eta = \dot{N}_{\mathrm{g}}/\dot{N}_{\mathrm{a}}$ and $\alpha = A_{\mathrm{eg}}/A_{\mathrm{ea}}$, where $\dot{N}_{\mathrm{g}}$ and $A_{\mathrm{eg}}$, $\dot{N}_{\mathrm{a}}$ and $A_{\mathrm{ea}}$ are the generation rates and amplitudes of electric flashes in a standard LS saturated with the given gas and with air, respectively, are given in Table 1.

5. Flash electroluminescence of organic liquid dielectrics has the following three characteristic features:

a) the luminescence has a flash character despite the continuous action of the excitation-energy source—a constant electric field;

**Fig. 2.** Dependences of the integral counting rate $\dot{N}$ of electric flashes on the voltage at the electrodes $V$ for a standard scintillator LS based on 1-methylnaphthalene with an addition of $0.02\,M$ acetic acid, saturated with xenon

(1), air (2), and hydrogen (3). Plane-parallel electrodes of stainless steel, $h = 4$ mm. Atmospheric pressure.

b) electric flashes are a threshold phenomenon, beginning when a certain voltage at the electrodes is reached;

c) electric flashes are observed in such liquids and solutions as luminesce weakly or do not luminesce at all under excitation by UV light or by ionizing radiation.

As is not difficult to see, flash electroluminescence of liquids differs substantially from their photo- or radioluminescence, but has an undoubted similarity to cavitation sonoluminescence. The latter also is a threshold phenomenon, beginning at ultrasonic powers sufficient for the onset of cavitation, and arises in nonluminescent liquids (for example, in water and $CCl_4$) ([11,12]). Moreover, an almost complete similarity is found in the influence of dissolved gases on electric flashes and on flashes of sonoluminescence (sonoflashes) in liquids. As is known, $H_2$ and $CO_2$ quench, while heavy noble gases enhance sonoluminescence, which is the glow of gases in cavitation cavities of liquids ([11,12]). On the other hand, dissolved gases affect the photo- and radioluminescence of liquids quite differently than they affect electric flashes. Of all the gases investigated, only oxygen is a quencher of the photoluminescence of aromatic substances in solutions ([13]). It is also well known that replacing dissolved air in any LS by any of the gases used, except oxygen, leads to the same increase in the amplitude of scintillations. Unlike the case of electric flashes, here the dissolved gases themselves have practically no effect on the yield of radioluminescence, but only displace dissolved atmospheric oxygen, which causes quenching ([10]).

**Table 1**

Influence of dissolved gases on the generation rate and amplitude of electric flashes in a liquid scintillator*

| Saturating gas** | $H_2$ | $O_2$ | $CO_2$ | Xe |
|---|---|---|---|---|
| $\eta = \dot{N}_g/\dot{N}_a$ | 0.01 | 0.04 | 0.76 | 2.7 |
| $\alpha = A_{eg}/A_{ea}$ | 0.34 | 0.33 | 0.25 | 1.37 |

* At a constant voltage of 20 kV on Rogowski electrodes of stainless steel with an interelectrode spacing $h = 4$ mm.
** At atmospheric pressure.

Thus, from experiments on the influence of dissolved gases on the flash electroluminescence of aromatic liquids and solutions, one may conclude that electric flashes arise not in the liquid phase at all, but in the gas phase.

6. We assume that electric flashes are formed during the development of electron avalanches arising as a result of electron emission into gas microcavities formed near microprotrusions on the cathode surface. In the vicinity of such microprotrusions, local electric fields may arise with strengths exceeding $\langle E \rangle$ by 1-2 orders of magnitude. Emission of electrons from a microprotrusion into the liquid, accompanied by local heating of the latter and by the formation, near the protrusion, of a cloud of negative ions, can apparently be the cause of a local rupture of the liquid and the formation around the protrusion of a microcavity, which is then filled with dissolved gas.

A more detailed description of the methodology for studying electric flashes and a discussion of the mechanism of their generation, with the inclusion of data on the spatial localization of the glow and on the distribution of potentials in the interelectrode gap, will be given in other papers.

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Received
1 VI 1967

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