AD-755 756

ELECTRIC STRENGTH OF LIQUID DIELECTRICS

I. Balygin

Foreign Technology Division
Wright-Patterson Air Force Base, Ohio

9 November 1972

DISTRIBUTED BY:

NTIS

National Technical Information Service
U. S. DEPARTMENT OF COMMERCE
5285 Port Royal Road, Springfield Va. 22151

FTD-HC-23-732-72

FOREIGN TECHNOLOGY DIVISION

1

AIR FORCE SYSTEMS COMMAND

ELECTRIC STRENGTH OF LIQUID DIELECTRICS

by

I. Balygin

D D C
RECEIVED
FEB 27 1973
B

Approved for public release;
Distribution unlimited.

UNCLASSIFIED
Security Classification

DOCUMENT CONTROL DATA - R & D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY (Corporate author)
Foreign Technology Division
Air Force Systems Command
U. S. Air Force

2a. REPORT SECURITY CLASSIFICATION
UNCLASSIFIED

2b. GROUP

3. REPORT TITLE
ELECTRIC STRENGTH OF LIQUID DIELECTRICS

4. DESCRIPTIVE NOTES (Type of report and inclusive dates)
Translation

5. AUTHOR(S) (First name, middle initial, last name)
Balygin, I.

6. REPORT DATE
1964

7a. TOTAL NO. OF PAGES
~~[illegible]~~ 321

7b. NO. OF REFS
326

8a. CONTRACT OR GRANT NO.

b. PROJECT NO.

c.

d.

9a. ORIGINATOR'S REPORT NUMBER(S)
FTD-HC-23-732-72

9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)

10. DISTRIBUTION STATEMENT
Approved for public release; distribution unlimited.

11. SUPPLEMENTARY NOTES

12. SPONSORING MILITARY ACTIVITY
Foreign Technology Division
Wright-Patterson AFB, Ohio

13. ABSTRACT

In this book account is given of the contemporary science of electric strength in liquid dielectrics. Experimental and theoretical data are presented on their breakdown. Processes connected with chlorodiphenyl are considered in a way which is useful for conditions which are encountered in application. Data are also presented on the electric strength of insulating mixtures and information on the change in the electrical and physical properties of certain insulation liquids subjected to radiation is also included. Furthermore, consideration is given to questions connected with the spark temperature at the time of an electric breakdown and the pressure in the discharge channel. The book is designed for specialists working in the area of the theory and application of liquid dielectric breakdown. It may also serve as a textbook for degree candidates and for technical institute students specializing in electrical insulation.

DD FORM 1 NOV 65 1473

UNCLASSIFIED
Security Classification

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Dielectric Breakdown						
Dielectric Strength						
Dielectric Property						

FTD-HC-23-732-72

EDITED TRANSLATION

FTD-HC-23-732-72

ELECTRIC STRENGTH OF LIQUID DIELECTRICS

By: I. Balygin

English pages: 313

Source: Elektricheskaya Prochnost Zhidkikh
Dielektrikov, 1964, pp. 1-227.

Translated Under: F33657-72-D-0854

Requester: AFWL/INP

Approved for public release;
Distribution unlimited.

THIS TRANSLATION IS A RENDITION OF THE ORIGINAL FOREIGN TEXT WITHOUT ANY ANALYTICAL OR EDITORIAL COMMENT. STATEMENTS OR THEORIES ADVOCATED OR IMPLIED ARE THOSE OF THE SOURCE AND DO NOT NECESSARILY REFLECT THE POSITION OR OPINION OF THE FOREIGN TECHNOLOGY DIVISION.	PREPARED BY: TRANSLATION DIVISION FOREIGN TECHNOLOGY DIVISION WP-AFB, OHIO.

FTD-HC-23-732-72 Date 9 Nov 19 72

ic

In this book account is given of the contemporary science of electric strength in liquid dielectrics. Experimental and theoretical data are presented on their breakdown. Processes connected with chlorodiphenyl are considered in a way which is useful for conditions which are encountered in application. Data are also presented on the electric strength of insulating mixtures and information on the change in the electrical and physical properties of certain insulation liquids subjected to radiation is also included. Futhermore, consideration is given to questions connected with the spark temperature at the time of an electric breakdown and the pressure in the discharge channel.

The book is designed for specialists working in the area of the theory and application of liquid dielectric breakdown. It may also serve as a textbook for degree candidates and for technical institute students specializing in electrical insulation.

TABLE OF CONTENTS

Foreword

The basic knowledge contained in the theory and application of liquid dielectric breakdown is usually presented in general courses in the technology of high voltage and the physics of dielectrics. There exist only three special books in the Russian language. The first of these was written by F.F. Vol'kenshteyn ("Breakdown in Liquid Dielectrics", 1934), and the second by A. Nikuradze ("Liquid Dielectrics", 1936, translated from the German). It is quite obvious that both of these have become obsolete. The third book by A.A. Andrianova and V.V. Skiteterova, "Synthetic Liquid Dielectrics" (1962), contains only a small number of data on electic strength.

A general correlation of the experimental and theoretical data on the question of breakdown in liquid dielectrics up to the year 1955 was performed by G.I. Skanavi in his book "The Physics of Dielectrics". Following the appearance of this book, a large number of articles were published in which new data on the regularities of breakdown in compressed gases, silico organic and polar insulating liquids were included. Moreover, in these articles information was communicated which was important for application and understanding of the mechanism of breakdown: this information pertained to the dependence of breakdown voltage on the dielectric constant, the structure of the molecule change and the electrode material, as well as to pre-breakdown and post-breakdown processes, to the spark temperature, to radiation stability, to mechanical stresses in the breakdown of liquids and so forth.

A more recent, but relatively compressed, systematization of literature sources on electric strength and conductivity in liquid dielectrics was given in a separate chapter of the book by G. Berks and G.G. Schulman in "Progress in the Field of

Dielectrics" (Volume I); in Russian this book was published in 1962.

Over the last several years, a large number of investigations on the breakdown of various liquids produced with short pulses of square form and with inter-electrode distances of several tenths of a micron have been accomplished. Interesting data have been obtained in these researches, but unfortunately they are not free from certain contraditions.

In the present monograph an attempt is made to generalize, correlate, and examine critically this and earlier material, in order to acquaint readers who are interested in the given problems with the present state of this area of interest.

The author requests that comments be addressed to the following: Leningrad D-41, Marsov Field, 1, Leningrad Department of the "Energy" Press.

CHAPTER I

Electric Strength, Chemical Composition, and Structure of Pure Liquids

1-1. Observations on the System of Units used in Measurement

The present monograph was written prior to the decision to introduce a new international systemof units known as (SI (International System). Therefore, the system in use with us up to 1963 is employed in this work.

At the foundation of the SI system, as is well known, there lie six basic units: the meter, the kilogram, the second, the ampere, the degree and the candela.

In the new system, for instance, temperature must be expressed in degress Kelvin (T° K). The relationship between this temperature scale and the ordinary one - the celsius (T° C) will be as follows: T° K = T° C + 273.15.

Pressure in the new system must be expressed in newtons (N) per square meter. One standard atmosphere, 1 at equals 9.80665 times 10^4N/M^2, and 1 MNHG = 1.33322N/M^2.

Density in the SI system is expressed in KG/M^3, specific gravity in N/M^3, and viscosity in M^2/sec and N times sec/N^2. One stokes (st) of kinematic viscosity will then be equal to 10^{-4} M^2/sec, and one poiz (pz) of dynamic viscosity will be equal to 0.1 N times sec/M^2.

X-ray and Gamma-ray exposure dose -- roentgens (R) in the new system will be equal to: 1R = 2.57976 times 10^{-4} Coulomb/kg. The unit of exposure dose power is R/sec = 2.957976 times 10^{-4} ampere/kg. Radiation of one curie is equal 3.7 times 10^{10} SI units.

1.2 On the Structure of Liquids

Before X-ray analysis came into use, the theory of the liquid state of substances was based on the concept, proceeding form the Van der Waal's equation, according to which the determined gradualness of the transition from the gaseous state to the liquid state was established. Under high compression the intermolecular forces of linkage between gas particles become so significant that the substance is already capable of preserving its volume by itself, independently from external pressure. A change in the aggregate state occurs and a liquid is formed which, according to these concepts, may be considered as a highly compressed gas.

However, X-ray analysis showed that condensed gas particles form small groups with ordered structure. This did not directly follow from the concept of a compressed gas, however, it was not excluded by that concept. Therefore, in the further development of knowledge of the liquid state the indicated concept was not wholly abandoned. From these same positions the metallic state of a substance may also be explained (L. 1-3).

If the electrons of individual atoms had a relatively weak coupling with the latter, then upon approach to distances comparable with the dimensions of electronic orbit a collectivization of these electrons must take place. Such a condition would be typical for metals. But in the case of strong couplings of electrons with the separate atoms of similar type the approach would not cause a collectivization of electrons, since their coupling with their own atoms is to some extent preserved. Then the substance would be a dielectric. Consequently the latter must consist of individual atoms whose strong fields retain their electrons. In the absorption of quanta of energy, for instance in irradiation, the electrons may leave the sphere of action of their atoms and form a conduction current.

In a similar type of irradiation it may turn out that the absorbed quantum of energy will be insufficient for complete detachment of an electron from its atom. The electron will go into an excited state, i.e., it will rotate around its atom in a larger orbit. In the collision of atoms, the excited state may be transferred to other atoms, i.e., excitons will be formed (L.4), but conduction will not occur. Such a phenomemon is observed in experiment and can easily be explained from the point of view of the classical concept, which is contained in the representation of a dielectric as a compressed gas. From the zone point of view the indicated phenomenon is difficult to explain.

At the present time, it is considered reasonable to think of a liquid at temperatures close to those at which crystallization occurs as having many more characteristics which are common with crystals than with gases, and at temperatures or pressures close to "critical" the liquid is more similar to a gas. Thus, the liquid state appears to be intermediate. The distinguishing features become especially conspicuous in the nature of thermal motion. In gases, the molecules move rapidly and in disorder, and the interaction of particles is initiated mainly in collision, which also impart to gases some of their characteristic features (diffusion, thermal conductivity and viscosity).

In solid bodies, the atoms complete their thermal oscillations over a long period in the same surroundings, but this environment is not constant: the atoms pass from one state of equilibrium to another (lattice points and interstices), and thus a continuous mixing of atoms takes place just as in gases, although slowly. In this respect we already see some common features in the similarity between a gas and a solid body.

For the motion of particles in a liquid there exists a significantly larger spaciousness than in the solid body, to the extent that, for instance, in the melting of crystals their volume increases by three to ten percent. However, the liquid particles, just as the particles of a crystalline body, perform their oscillations around a temporary equilibrium position. If it acquires sufficient energy the liquid particle leaves its position and transfers to a new position. Such transitions happen very often and in this respect liquids differ substantially from solid bodies. In transition resulting from thermal motion microcavities may be formed spontaneously in liquids on account of the expansion of particles to the sides (the process of cavitation). These cavities, as one may surmise, play a certain role in the spread effect in determining the values of breakdown voltages, a circumstance which is ordinarily ascribed to the effect of impurities and to certain random factors.

The duration of oscillation of liquid particles in the vicinity of one equilibrium position depends on temperature. Upon increase in the latter this number of oscillations diminishes. For instance, water particles near a fixed equilibrium position at room temperature manage to complete about one hundred oscillations.

In the case of gases and liquids the forward motion of particles occurs in zigzag fashion, but the difference is contained in the fact that with each change in direction of motion the liquid particles come to a standstill, at which time they behave in such a fashion that it appears that they belong to a solid body.

In the study of the regularities of scattering of X-rays by liquids well-defined, although washed out, maxima in the scattered irradiation were detected (L.5). Based on this finding one may propose the existence of some ordering in the structure of liquid bodies. In monotomic liquids such as mercury, gallium and thallium, three or four clearly expressed maxima are found for each; in the X-ray photographs of liquid sodium there is only one.

In the X-ray photographs of fatty acids and alcohols two such maxima are observed apiece. The first maximum coincides with that which is observed in the same substances in the solid, crystallized state, and the second is caused by the lateral dimensions of molecules in the form of sufficiently long chains.

In liquid mixtures consisting of benzine and cyclohexane X-ray analysis reveals a separation of the maxima in the scattered ray intensity. This must indicate that the molecules are collected in separate groups and in the mixture preserve these groups by the same processes as in the separate components. The same effect is observed also in the mixing of phenol with water.

In this way one may consider the existence of micro-volumes with ordered structure in liquids to be established. In this respect a liquid also bears a definite resemblance to a solid body It turns out that against the background of general disorder liquids have however a definite order in their arrangement at small distances (near order).

X-ray analysis, however, does not provide the capability of determining the nature of such quasi-crystalline groups to the degree to which this may be done for crystals. At the present time one may state two hypotheses on the nature of these formations.

According to the first of these in micro-volumes with dimensions of 10 - 20 A° there is a definite ordered structure of scattering centers, with a remarkably strong suggestion of crystalline structure. Based on this representation a liquid may be considered as consisting of a very large number of shallow crystolites separated by amorphous layers.

According to the second hypothesis, the molecular ordering of liquids corresponds to the so-called cybotactic state. At a given moment of time, a liquid may be represented also as consisting of small ordered groups. But the molecules in these cybotactic groups are not strongly attached, and they are constantly shifting. As a matter of fact, the groups do not exist for an extended period of time, but disintegrate and are created anew. This fact sets cybotactic apart from crystolites of solid material (L.6). With a change in temperature the structure of cybotactic may also change. With an approach to the crystallization point, as a result of the action of forces accounting for the crystalline construction, the structure of these groups may become near to crystalline. This fact is confirmed also by the data of X-ray analysis. The scattered ray intensity curves in liquids at a temperature close to the crystallization point are seen to be similar to the corresponding curves for the solid crystalline state. Apparently also the average arrangement of scattering centers in liquids becomes the same as in a crystal.

The presence of cybotactic groups has been established in liquid paraffins (L.7 and 8). It turned out that for such liquids molecule chains of 21 to 29 carbon atoms at a temperatures close to the melting point are arranged in parallel fashion. In a plane perpendicular to the axes of the chains the molecules are densely packed, and each one may be considered as a cylinder with cross-sectional diameter of 4.74 A°. Experiments showed that in many cases where the structure has been changed, the electrical and physical properties of the liquid have also been altered.

According to data (L.9), liquid sulfur at a temperature of 220°C undergoes significant structural changes in almost jump fashion. At this same temperature its breakdown voltage (E_{br}) also changes radically; it reaches its highest value of 0.07mv/cm (L.10).

Concerning water it is known that at low temperatures it has the crystalline structure of tridymite (form one). At ordinary temperatures the crystolites has the structure of quartz (form two), and at elevated temperatures water appears as a densely packed, ideal liquid (form three) (L.11 and 12). With a change in temperature these forms pass from one into the other. The transition of a form one group into form two or three is accompanied by an increase in forward and rotational motion of the molecules.

The breakdown voltage of water at temperatures below zero is almost unaltered, but at 0°C it drops discontinuously by a factor of almost two (L.13).

When gases are compressed and cybotactic groups are formed E_{br} in some cases rises sharply. For instance, E_{br} of liquid argon is equal to about 1mv/cm (L.14 and 15). The corresponding value for gaseous argon at room temperature is less than 0.032mv/cm. For other substances in a transition from one aggregate state to another E_{br} changes smoothly, for instance with carbon dioxide gas (L.16).

From the data presented it follows that the breakdown voltage of liquids depends on their structure and that it is impossible to predict beforehand the nature of a change in E_{br} in a transition of substances from the gaseous state to the liquid state. The basic electrical properties of liquids are apparently determined by "near order", i.e., by the nature of the interaction of molecules with near neighbors, as takes place with semi-conductors (L.17).

Experiments show that for isomers of certain liquid dielectrics with various molecule chain structures the values of E_{br} are also not the same. When side chains are present E_{br} drops noticeably (L.18). In this connection it is interesting to note that according to the data (L.19), the addition of a CH_3 group or an OH to the side of the chain increases the transverse dimension of the molecules by approximately 0.6 and 0.4A° respectively.

A more detailed account of the relation between chemical composition of liquid and their structure will be presented in the following paragraphs.

1-3 The Dependence of Breakdown Voltage on the Density of Liquids

In the investigation of hydrocarbon liquids of the paraffin series it was noted that their breakdown voltage became higher as the density increased. The question arises as to the extent to which this regularity holds in general for liquid dielectrics. Is it in reality true only for one homogolous series, in which hydrocarbons with the same construction $C_nH_{2n} + 2$ differ only in the length of the molecule chain, or may it be extended to insulating liquids with another chemical composition and structure?

According to the data of references (L.18, 20, 21, 22, and 23), it may be confirmed that at least for the paraffin series of hydrocarbons this regularity is applicable in full degree. However, in the following paragraph it will be shown that the given confirmation is not very rigidly grounded. It is necessary to note that investigations of the indicated liquids were carried out with quite small spark gaps and short pulses. On the basis of the experimental material it was also shown that in order to determine E_{br} of the liquids one may use a somewhat modified paschen law, according to which $E_{br} = F(P,1)$ where P is the pressure and 1 is the distance between electrodes.

The liquids under investigation were carefully purified and filtered. Particular attention was devoted to the removal of impurities of unsaturated hydrocarbons with a different specific gravity, and also hydrocarbons with an admixture of sulfur and suspended solids. Therefore the liquids were washed several times with concentrated sulfuric acid. Some of the experiments were carried out with a mercury cathode. The liquids investigated in this way over the course of several days were mixed with mercury in order to prevent the possible formation of contaminated film on the cathode surface. The anode, made of stainless steel, was thoroughly polished. The amplitude of rectangular pulses was gradually increased up to breakdown. Motion of the mercury cathode under an imposed voltage was also taken into account (L.23). The dependence of E_{br} on the liquid density D, as determined from the data is shown in Figure 1. It turned out that with an increase in D the breakdown rises linearly. This regularity was corroborated even more thoroughly by experiments conducted with highly polished hemispherical electrodes of stainless steel. The investigations were performed in a teflon vessel with glass windows for observing the spark gap. In these experiments particular attention was devoted to the removal of finely suspended impurities. The distance between electrodes in all cases was equal 5 times 10^{-3}. The data obtained are presented in table 1.

As one would expect, with a reduction in the pulse duration or in the time of voltage application the values of E_{br} increase noticeably. According to the data of (L.24), such a linear dependence has been established also with dc voltage (see curve 4 of Figure 2). It has turned out that with some assumptions all of this may be put on theoretically firm ground. But according to other sources in the literature such a linear dependence between E_{br} and the density of liquid hydrocarbons does not exist. Other confirmation of a similar type is considered to rest on firmer ground. This will be discussed in more detail in a subsequent paragraph.

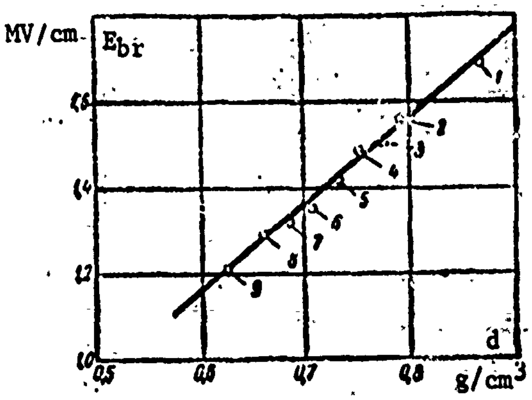


Fig. 1. The dependence of E_{br} on the density of hydrocarbons in the paraffin series. 1-mineral oil; 2-decane + mineral oil; 3-hexadecane; 4-N-dodecane; 5-N-decane; 6-N-octane; 7-N-heptane; 8-N-hexane; 9-N-pentane.

Formally liquid hydrocarbons may be considered as gases compressed under a pressure of about 2,000 atm. The breakdown voltage of, for instance, air is equal to about 0.032 mv/cm. Therefore, E_{br} of liquids, according to the Paschen law, would have to be about 2,000 times greater. On the contrary, they break down at $E = 0.1$ to 5.0mv/cm (L.25). Consequently the Paschen law must actually be modified somehow in order to explain the indicated linear dependence.

In gas spark gaps the electrons transfer the energy obtained from the applied field to molecules of the medium through collisions. This energy is expended in the excitation of electrons in molecules, in the dissociation of the latter, radiation, shocks of the second kind and so forth. In order to form a streamer it is necessary that free electrons obtain more energy from the field than they lose through collision.

Table 1

Breakdown Voltage of Liquid Hydrocarbons Subjected to Rectangular Pulses

Hydrocarbons	Density g/cm^3	Duratio of rec pulses micro-sec	Break-down voltage MV/cm
N-pentane	0,626	1,40	1,11
N-hexane	0,659	0,25	1,89
»	0,659	0,50	1,73
»	0,659	0,70	1,63
»	0,659	1,40	1,55
»	0,659	5,00	1,54
N-heptane	0,684	1,40	1,66
N-octane	0,703	1,40	1,79
N-nonane	0,718	0,25	2,07
»	0,718	0,50	1,91
»	0,718	0,70	1,88
»	0,718	1,40	1,83
»	0,718	5,00	1,81
»	0,718	11,00	1,83
N-decane	0,730	1,40	1,92
N-tetradecane	0,762	1,40	2,00

In condensed phases the energy is expended mainly in the excitation of oscillations in the atoms of the molecules. When the molecules approach each other, as a consequence of the mutual effect of their micro-fields, the dissociation energy decreases. Therefore one may suppose that in the excitation of electrons in the molecules many of them dissociate. This situation apparently is one of the reasons for the deviation from the Paschen law with respect to the reduction in value of E_{br} for liquids.

In reference (L.21) it is taken for granted that the mean free path of electrons depends on the number of hydrogen and carbon atoms occurring in one cubic centimeter of liquid:

$$\frac{1}{\lambda} \approx \sum n_i a_i = n_C a_C + n_H a_H, \quad . \quad (1)$$

where n_i is the number of i-type atoms in a unit of volume (carbon atoms n_c and hydrogen n_h), and a_i is a constant with the dimension of area.

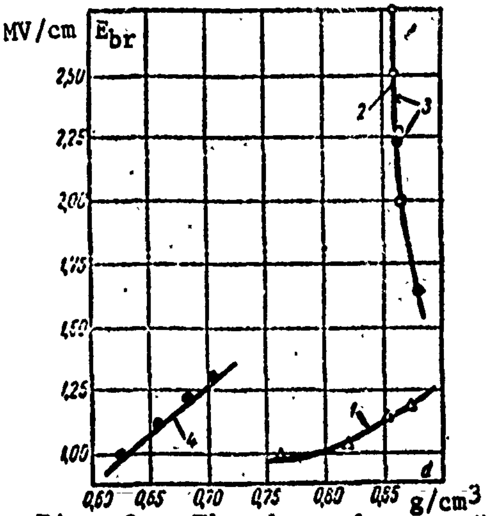


Fig. 2. The dependence of E_{br} of various liquids on their density: 1-silico organic liquids; 2-aromatic hydrocargons with unbranched chains; 3-the same, but with branched chains; 4-hydrocarbon liquids of the paraffin series with straight chains and with dc voltage.

The energy of an electron, obtained by it in a path length from the applied field is equal to $Ee\lambda = W$. Therefore the authors of reference (L.21) under simplifying assumptions consider that:

$$E_{np} \approx \frac{bW_0}{\lambda}, \quad (2)$$

where W_0 is the energy of free electrons for which their losses at the moment of collision are greatest, and B is a proportionality factor.

Under the condition where W_0 for carbon and hydrogen atoms is the same and where it remains constant with a change in λ, one may write from (one) and (two):

$$E_{np} = BW_0(n_H a_C - n_H a_H). \quad (3)$$

In agreement with this formula the breakdown of liquid hydrocargons must in fact be connected with the density by a linear law. Supplementary data on this question will be presented in Article 10-3.

A verification of the applicability of the aschen law was attempted in (L.26) for gas-phase and liquid-phase carbon dioxide. Breakdown was produced between steel spheres with thoroughly polished surfaces. The CO_2 gas was compressed in a compressor and its density was varied over a range from 0.4 times 10^{-3} to $0.2 g/cm^3$. At higher pressures a liquid was formed.

It turned out that the paschen law was valid in the gas phase for interelectrode distances of L greater than 0.25 mm, and in the formation of breakdown shock ionization occurs. For smaller values of L deviations from this law are observed, and in the passage to the liquid state it is no longer fulfilled.

Data from measurements of U_{br} for direct-current voltage and L=0.19mm are presented in Figure 3. Abrupt changes in U_{br} in passage from the gaseous state to the liquid state are not detected. In the condensed phase the growth in U_{br} for an increase in density takes place significantly more slowly; the linear dependence is destroyed.

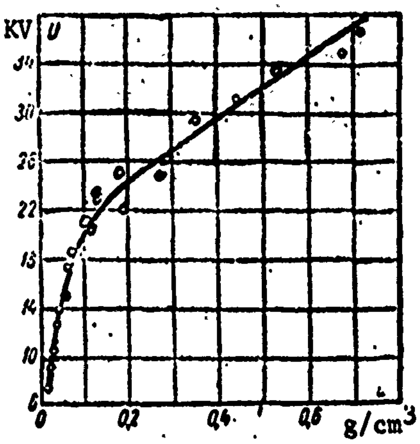


Fig. 3. The dependence of E_{br} of carbon dioxide on density.

Therefore, the conclusion may be drawn that even the modified Paschen law for gases may apparently by employed for a definite of liquid hydrocarbons.

The linear dependence of E_{br} on density is not revealed for insulating liquids with different chemical composition and structure. Moreover it turns out that the opposite relationship also exists as, for instance, for some aromatic hydrocarbons.

A curvilinear dependence of E_{br} = F (for DC voltage) and interelectrode distance (uniform field) of L = 8 times 10^{-3}cm is found for a silico-organic liquid (see Articles 2-2 and 3-2), as is apparent from curve one in Figure 2 (L.27). Curve two of this drawing is recorded for an investigation of aromatic hydrocarbons for which an increase in density D causes a sharp reduction in the value of E_{br} (see Table 2).

These data were obtained for rectangular pulses of duration of 1,65 microseconds and for interelectrode distances of about 51 microns. Prior to the experiment the liquids were distilled and filtered through a glass filter (L.28).

With respect to the dependence of E_{br} = F(d) it pays to note that for aromatic hydrocarbon liquids E_{br} does not depend on the branching of chains of molecules. This is apparent from the experimental points notated number 3 in Figure 2. In the breakdown of longer gaps a definite dependence of E_{br} = F(d) is not revealed for fluoorganic liquids (see Table 3). In this table, in addition to E_{br} and d, some other parameters are presented which characterize the indicated liquids. Their resistivity is about 10^{14} to 10^{15} ohm/cm, and the tangent of delta at a frequency of 100 hertz is less than 5^{-4}.

TABLE 2

Breakdown Voltage of Aromatic Liquid Hydrocarbons

Name of Liquid	Density g/cm^3	Breakdown voltage MV/cm
Benzene	0,879	1,63
Methylbenzene	0,866	1,99
Ethlybenzene	0,867	2,26
N-propylbenzene	0,862	2,50
Isopropylbenzene	0,861	2,35
N-butylbenzene	0,862	2,78
Isobutylbenzene	0,857	2,22

The smallest value D = 1.69 for $C-C_6S_{12}O$ corresponds to E_{br} = o.164 mv/cm, and the lowest E_{br} = 0.14 mv/cm was found for $C-C_8F_{16}$ with D - 1.84.

It is appropriate to note that liquids of similar type are non-flammable, explosion-proof and chemically inert.

Thus, if we consider liquid dielectrics in general, no definite dependence of E_{br} on density has been established for them so far.

1-4. The Influence of Some Structural Factors on the E_{br} of Liquids

In article 1-2 it was shown that the addition of CH_3 or OH chains onto the side increase the dimensions of molecules roughly by 0.6 and 0.4 A respectively. This situation must be taken into account in Equation (1) by the coefficient a, which has the dimensions of area, as was mentioned in the preceding paragraph. Therefore, for liquid hydrocarbons with branched molecule chains, according to Formula (2), E_{br} would

TABLE 3

Some Electrical and Physical Properties of Fluorganic Liquids

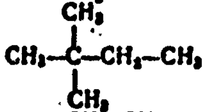
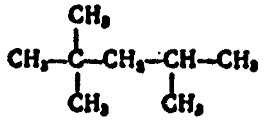
Chemical Composition of Liquids	Density g/cm^3	Break-down voltage MV/cm	Dielectric permotivity	Boiling temp. °C	Melting temp. °C
$(C_4F_9)_3N$	1,87	0,180	1,86	178	—50
$c-C_8F_{16}$	1,84	0,140	1,75	101	—
$(C_3F_7)_3N$	1,82	0,176	1,85	129	—
$(C_6F_{13})_2O$	1,81	0,180	1,85	172	—90
$c-C_8F_{16}O$	1,77	0,172	1,85	103	Less than—100
$(C_2F_5)_3N$	1,73	0,156	1,85	129	—
$(C_4F_9)_2O$	1,71	0,172	1,77	101	—
$c-C_6F_{12}O$	1,69	0,164	1,85	56	—

have to be larger than for liquids with the same density, but with unbranched chains. However, experiments do not confirm this conclusion.

The liquids under investigation were purified with concentrated sulfuric acid, washed, dried and filtered (L.23). Breakdown occurred when voltage pulses of duration 1.4 microseconds were fed to the dielectric. The measured values of E_{br} are presented in Table 4. Along with it, some other data are presented which characterize the liquids under examination.

TABLE 4

Data on E_{br}, Molecular Weight and Molecular Structure of Liquid Hydrocarbons

Hydrocarbons	Breakdown voltage MV/cm	Molecular weight	Chemical formula	Chain Structure
N-pentane	1,44	72,146	C_5H_{12}	$CH_3-CH_2-CH_2-CH_2-CH_3$
N-hexane	1,55	86,172	C_6H_{14}	$CH_3-CH_2-CH_2-CH_2-CH_2-CH_3$
N-heptane	1,66	100,198	C_7H_{16}	$CH_3-(CH_2)_5-CH_3$
N-octane	1,79	114,224	C_8H_{18}	$CH_3-(CH_2)_6-CH_3$
N-nonane	1,83	128,250	C_9H_{20}	$CH_3-(CH_2)_7-CH_3$
N-decane	1,92	142,276	$C_{10}H_{22}$	$CH_3-(CH_2)_8-CH_3$
N-tetradecane . .	2,00	198,380	$C_{14}H_{30}$	$CH_3-(CH_2)_{12}-CH_3$
2-methylpentane .	1,49	86,172	C_6H_{14}	 $CH_3-\underset{CH_3}{\underset{\vert}{CH}}-CH_2-CH_2-CH_3$
2.2-dimethylbutane	1,33	86,172	C_6H_{14}	 $CH_3-\overset{CH_3}{\overset{\vert}{\underset{CH_3}{\underset{\vert}{C}}}}-CH_2-CH_3$
2.3-dimethylbutane	1,38	86,172	C_6H_{14}	 $CH_3-\overset{CH_3}{\overset{\vert}{CH}}-\overset{CH_3}{\overset{\vert}{CH}}-CH_3$
2.4 dimethylpentane	1,44	100,198	C_7H_{16}	 $CH_3-\underset{CH_3}{\underset{\vert}{CH}}-CH_2-\underset{CH_3}{\underset{\vert}{CH}}-CH_3$
2.2.4-trimethylpentane	1,40	114,224	C_8H_{18}	 $CH_3-\overset{CH_3}{\overset{\vert}{\underset{CH_3}{\underset{\vert}{C}}}}-CH_2-\underset{CH_3}{\underset{\vert}{CH}}-CH_3$

From Table 4 it is seen that, in addition to normal N-hexane, three of its isomers were also investigated. The chemical formula and molecular weight of these are indentical, but the structure of the molecule chains is different. Side branching is absent in the N-hexane chain, and its E_{br} = 1.55 mv/cm. The isomer 2-methylpentane has one side-branched, and its E_{br} = 1.49 mv/cm. For the remaining two isomers with two side branchings the values of E_{br} are still less. In Article 10-2 it will be shown that this condradiction will be removed if we consider not the whole molecular, but separate groups within it (CH, CH_2, CH_3).

From the experiments it follows that for isomers of the homologous series the breakdown voltage rises with an increase in density both for pulsed (Fig. 4) and for DC voltages. For aromatic hydrocarbons, as was mentioned in the preceding paragraph the breakdown voltage does not depend on the type of molecule chains.

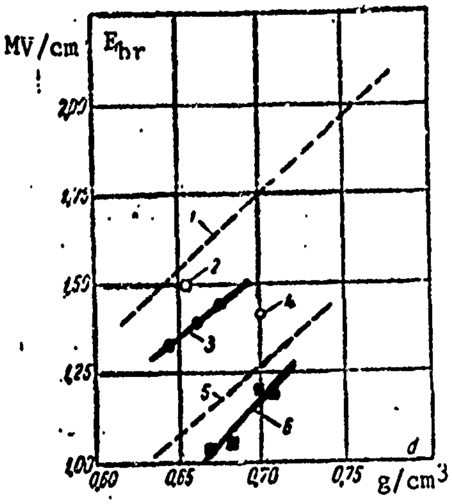


Fig. 4. Breakdown Voltage of Liquid Hydrocarbons.

1- with straight molecule chains for pulsed voltage; 2- the same, but with 1 branching; 3- the same, but with 2 branchings; 4- the same, but with 3 branchings; 5- with straight molecule chains, but for DC voltage; 6- the same, but with 1 branching.

Experiments also showed that in the gas phase the four isomers of hexane have the same E_{br}. The boiling temperature of N-hexane = 68.74 C; 2-methylpentane it is 60.27 C;

2,2-dimethylbutane 49.74 C; and 2,3-dimethybutane 59.99 C. In the gas phase the side chains have no effect on E_{br}. This situation testifies to the difference in the mechanisms of breakdown formation for gases and for liquids.

In connection with the statements made on the influence of the structure of molecule chains on E_{br} for liquid hydrocarbons it is interesting to compare also the effect of other physical and chemical parameters. Data of this type are presented in Figure 5 (L.29 and 30). Here, along the abscissa in addition to the density D and molecular weight M, found already in Tables 1 and 4, the following are also plotted: heat of evaporation Q_{ev}, boiling temperature T_b, surface tension γ, viscosity eta and the thermodynamic potential ΔZ (L.31 and 32).

With an increase in almost all of the enumerated parameters, except for the thermodynamic (isobaric) potential, the value of E_{br} of liquid hydrocarbons of the paraffin series rises. To the extent that these parameters characterize the strength of the inter-molecular bonding, the authors of the references (L.29 and 30) have drawn the conclusion that electrical breakdown is apparently somehow connected with a surmounting of the inner-molecular forces of coupling. Some considerations pertinent to this question will be presented in Article 5-1. But the isobaric potential characterizes the bonding strength of chemical compounds. On this basis a second conclusion is drawn, namely that the indicated strength does not determine the magnitude of the breakdown voltage. The effect of inter-molecular bonds may be realized also through the interaction of accelerating electrons with oscillating molecules or groups of atoms in the liquids.

In the temperature interval from the melting point to the boiling point certain physical, chemical and structural parameters of the liquids undergo significant changes. Therefore, their electric strength must also change. Their dependences on temperature will be discussed in detail in Article 4-1.

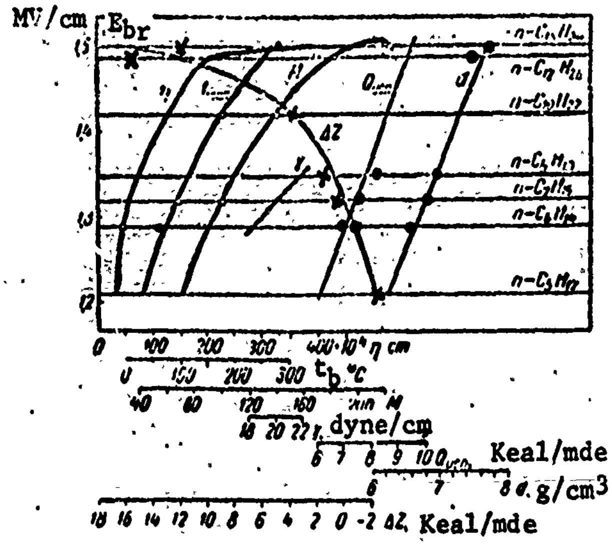


Fig. 5. The Dependence of E_{br} of Liquid Hydrocarbons of the Paraffin Series on Certain Physical and Chemical Parameters.

Here we will present only certain data which have relevance to the question of present interest. They were obtained in an investigation of liquid hydrocarbons which were also very well purified. Breakdown was produced at various temperatures and at constant voltage. A distance between electrodes of 3 times 3^{-3} cm was not changed during the experiment.

The curves of Figure 6 represent the dependence of Log E_{br} on temperature (1,000/T). In light of the character of the change of these curves one may reach a conclusion concerning the existence of two so to speak special points. The first inflection point corresponds approximately to a temperature of 40 C, and the second occurs at about -20 C. In the interval from -60 to -20 C the values of E_{br} fall abruptly, and within the limits from -20 to +40 C they barely change. Further decrease in E_{br} is observed at temperatures above 40°C. These features are explained in (L.33) by changes in the oscillational condition of molecule chains in the materials under study.

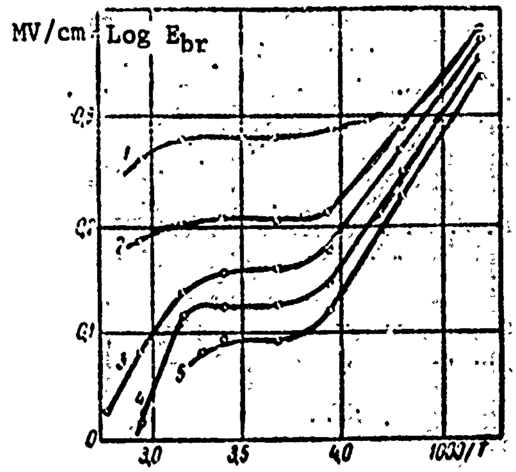


Fig. 6. The dependence of log E_{br} of liquid hydrocarbons of the paraffin series on temperature on an absolute scale (1000/T).
1 - $C_{10}H_{22}$; 2 - C_8H_{18}; 3 - C_7H_{16}; 4 - C_6H_{14}; 5 - C_5H_{12}

In the case where the action of a constant is involved and the electric field is directed along the chain, a polarization of the molecules must take place. Inelastic collisions with electrons with such polarized centers will occur more frequently. In this situation the electrons accelerated by the imposition of a field will lose energy, and the breakdown voltage of the liquids must be relatively high.

The orientation of molecules which have been polarized under conditions of a temperature elevation from -60°to -20°C will be partially destroyed by the more vigorous thermal oscillation. Collisions of electrons will become more infrequent, and consequently energy losses will be reduced. Therefore, the breakdown voltage must decrease. In this way the sharp drop in E_{br} from the left of Figure 6 is explained.

A further increase in temperature from -20°to +40°C leads to a still greater undoing of the orientational order, but in this process the oscillations of the molecule chains will exert an influence. Therefore, in the given region of temperature change two oppositely acting factors must have an effect on E_{br}. Therefore, the values of E_{br} at the indicated temperatures hardly change.

At still higher temperatures (greater than 40°C) the state of the molecules will be characterized by an ordered rotational motion of the chains around the longitudinal axes and the number of collisions of electrons will decrease. The orientational order will be destroyed even further and the values of E_{br} will again decrease.

In the case of the heating of liquids to temperatures close to the boiling point, gas bubbles will begin to form. The ionization processes in these must facilitate a gradual development of breakdown with still lower voltages.

For the purposes of the discussion of breakdown criteria which has been presented the following equation (L.33) is proposed:

$$E_{br} = kN\Sigma n_i Q_i \qquad (4)$$

where N is the number of molecules in one cubic centimeter; N_i is the number of i-type groups with a "cross-section" in each molecule, where the collision of electrons in vibrating centers Q_i is probable; k is a constant which may be determined from the experiment.

It is assumed that the electrons travel freely without collisions over an average distance λ, depending on the density of the liquid. With a rise in temperature the density decreases and λ increases. Therefore, E_{br} must decrease.

In order to clarify the role of structural factors the effect of density may be excluded. For this purpose it is sufficient to construct curves of the dependence of $E_{br}/N = F(T)$, where N is also the number of molecules in one cubic centimeter. If only the density of the liquids exerts an influence on the reduction in E_{br}, then the values of E_{br}/N do not have to depend on temperature. Curves of this type are presented in Figure 7, and one may isolate three regions with the characteristic temperatures T_0 and T_k. Their values agree closely with those found previously from the curves of Figure 6. From this it follows that only the density of liquids can be said not to be a dertermining factor for E_{br} even for liquid hydrocarbons of the paraffin series.

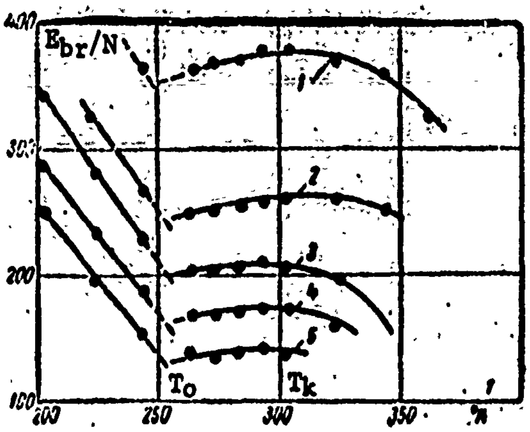


Fig. 7. The dependence of E_{br}/N on temperature. For identification of curves see Figure 6.

1-5 The Relation Between E_{br} and the Dielectric Permittivity of the Liquids

It is well known that with a prolonged imposition of voltage and with inter-electrode distances of greater than fractions of a millimeter E_{br} of highly polarized liquids is relatively small. In reference (L.34) it is shown that the dielectric permittivity (dielectric constant) of liquids ε is connected with E_{br} by a fully determined specified dependence: with an increase in ε, E_{br} decreases.

Experiments were carried out with DC and AC (50 hertz) voltages. At atmospheric pressure and at essentially room temperature breakdown occurred in gaps no smaller than fractions of a millimeter. Therefore, the values of E_{br} which were obtained were not so high as in experiments described in references (L.23, 24, and others). A voltage rise with a rate of 1kz/sec. was effected. In order that the electrodes might be easily controlled, they were fastened to polished surfaces in a glass vessel. In order to remove traces of salts and acids from the liquids, they were washed several times with distilled water. Chromous and bromide compounds were dried with calcium chloride, and the pure hydrocarbons were dried with phosphorous pentoxide. The drying of siloxane was accomplished with sodium sulfate. In addition the liquids were twice distilled with a very low rate of drop formation.

With DC voltage only non-polar liquids experienced breakdown, but for polar with this voltage with breakdown yet to occur, a vigorous motion was observed which facilitated the appearance of gas bubbles. The values of E_{br} as recorded are too low. Therefore, polar liquids were investigated with AC voltage at 50 hz. In the absence of intense motion the values of E_{br} for DC and AC voltages coincided. The dielectric constant was measured at a frequency of one megahertz.

It is known that for every breakdown in liquids there occur certain reverse changes: complex molecules disintegrate into simpler ones, gaseous products and new molecules are formed, and the number of ions grow. If the discharged current is not limited and if the discharge is not cut off immediately after completion of breakdown by shunting of the specified gap, then after the first and the following (second) breakdowns E_{br}, as a rule, decreases. This reduction is especially noticeable in the case where the quantity of liquid under study is small. In the vessel, there is formed something which can be considered as a mixture of liquid and the products of its decomposition. These conditions were met in those experiments which were analyzed. Therefore, only those values of E_{br}, which were determined in the first breakdowns (the average values from three separate tests) were taken as genuine.

It turned out than in breakdown the destructive processes for various liquids were not the same, and from the degreee of dissociation one may determine their stability in relation to the breakdown action. It was convenient to characterize this value R by the reduction in value of E_{br} after six breakdowns following one after the other in the same trial of one liquid.

In Table 5 the values of E_{br} for the first and sixth breakdowns of 33 insulation liquids with various chemical compositions and structures are presented. In addition, some other data characterizing the liquids under investigation have been collected in the same table.

According to the data of the table the values of E_{br} of the liquids under study varied within the limits of 0.868 to 0.182 mv/cm, the values of the dielectric constants varied from 1.88 to 15.06. The magnitude of R varied at the same time within the limits 0.96 to 0.2 times E_{br}. For some liquids a significant reduction in E_{br} was observed already after the second breakdown, but there were also liquids for which this did not happen even after the sixth breakdown. In this category we may include carbon tetrachloride (CCl_4)(curve 1, Figure 8). For methylenechloride (CH_2CL_2) R is small (curve 3). The drop in E_{br} is plotted along the ordinate axes of Figure 8 in percent. Diethyl-

TABLE 5

Certain Electrical and Physical Properties of Insulating Liquids

Name of Liquid	Chemical Formula	Breakdown Voltage MV/cm.	E_{br} after six breakdowns related to first.	Density of Liquids at 20 C g/m^3	Dielectric constant at 20 C
Hexachlorbutadiene	$Cl \cdot CCl : CCl_2$	0,890	--	1,6898	2,55
Diethylether	$(C_2H_5)_2O$	0,589	0,96	0,7137	4,38
Hexamethyldicyloxane	CH_3Si_2O	0,820	0,96	0,7610	2,15
Octamethylcyclotetraciloxane	$[(CH_3)_2SiO]_4$	0,790	0,94	0,9567	2,40
Carbon tetrachloride	CCl_4	0,810	0,93	1,5937	2,24
1.1.2.2-tetrabromoethane	$Br_2HC \cdot CHBr_2$	0,420	0,90	2,9638	6,70
N-hexadecane	$C_{16}H_{34}$	0,828	0,80	0,7751	2,04
N-haptane	C_7H_{16}	0,840	0,78	0,6838	1,93
N-hexane	C_6H_{14}	0,868	0,74	0,6595	1,88
1.1.2.2-tetrachloroethane	$Cl_2HC \cdot CHCl_2$	0,355	0,72	1,6025	8,08
1,2-dibromoethane	$BrH_2C \cdot CH_2Br$	0,552	0,71	2,1771	4,73
Chloroform	$CHCl_3$	0,545	0,65	1,4889	4,89
Benzine	C_6H_6	0,781	0,61	0,8789	2,28
Methylcyclohexane	$C_6H_{11}CH_3$	0,822	0,63	0,7693	2,24
2,2-dimethylpentane	$CH_3 \cdot (CH_2)_2 C (CH_3)_2 CH_3$	0,846	0,62	—	1,97
Paraldehyde	$[CH_3CHO]_3$	0,182	0,60	1,0077	15,06
Cyclohexane	C_6H_{12}	0,830	0,58	0,7785	2,04
Pentachlorethane	$Cl_2HC : CCl_3$	0,635	0,57	1,6881	3,76
Trichloroethylene	$Cl_2C : CHCl$	0,670	0,55	1,1655	3,44
Bromobenzine	C_6H_5Br	0,499	0,54	1,4951	5,31
Toluene	$C_6H_5CH_3$	0,786	0,53	0,8556	2,39
(cis) 1.2-dichloroethylene	$ClHC : CHCl$	0,317	0,52	1,2500	8,92
Chlorobenzine	C_6H_5Cl	0,499	0,51	1,1062	5,54
1.2.4-trichlorobenzine	$C_6H_3Cl_3$	0,620	0,50	1,4660	3,98
1.2-dichloroethane	$ClH_2C : CH_2Cl$	0,275	0,47	1,2600	10,03
Tetrachloroethylene	$Cl_2C : CCl_2$	0,776	0,45	1,6070	2,46
Propylbromide	$CH_3CH_2 \cdot CH_2Br$	0,370	0,41	1,3597	7,66
Propylchloride	$CH_3CH_2 \cdot CH_2Cl$	0,350	0,43	0,8923	8,13
M-dichlorobenzine	$C_6H_4Cl_2$	0,538	0,43	1,2820	4,90
O-dichlorobenzine	$C_6H_4Cl_2$	0,312	0,43	1,3281	9,43
(trans) 1.2-dichloroethylene	$ClHC : CHCl$	0,815	0.40	1,2502	2,18
Methylenechloride	CH_2Cl_2	0,325	~0,3	1,3258	8,56
1.1-dichloroethylene	$Cl_2C : CH_2$	0,506	~0,2	1,2500	4,82

ether $(C_2H_5)_2O$ and hexamethyldicyloqxane (CH_3SI_2O) should be considered as the most reliable among the liquids tested (see Table 5). For molecules with oxygen bonds the stability appeared to be higher. Pure saturated hydrocarbons also possessed a relatively high stability.

It was noted that liquids with molecules in the form of a ring were less stable than those with chain structure. For instance:

$$R\,[(\mathrm{CH_3})\,\mathrm{CHO}]_3 < R\,(\mathrm{C_2H_5})_2\mathrm{O};$$
$$R\,[(\mathrm{CH_3})_2\,\mathrm{SiO}]_4 < R\,(\mathrm{CH_3})_6\,\mathrm{Si_2O};$$
$$R\,(\mathrm{C_6H_{11}CH_3}) < R\begin{cases} n\text{-}\mathrm{C_{16}H_{34}}; \\ n\text{-}\mathrm{C_7H_{16}}; \\ n\text{-}\mathrm{C_6H_{14}}. \end{cases}$$

For the first inequality the curves of the decrease in value of E_{br} are presented in Figure 9. Besides, it turned out that the reliability of liquids with straight chains was greater than those with branched chains:

$$R\,(2.2\text{-}\mathrm{C_7H_{16}}) < R\,(n\text{-}\mathrm{C_7H_{16}}). \qquad (25A)$$

It was also established that the stability of liquids with chlorine derivation was smaller than that of liquids of bromine derivation:

$$R\,(\mathrm{Cl_2HC{\cdot}CHCl_2}) < R\,(\mathrm{Br_2HC{\cdot}CHBr_2}), \qquad (25B)$$

but for the majority of liquids with symmetric molecular structure R was always greater regardless of the dependence on chlorine or bromine content in comparison with the asymmetric construction:

$$R\,(\mathrm{Cl_2HC{\cdot}Cl_3}) < R\,(\mathrm{Cl_2HC{\cdot}CHCl_2}). \qquad (25C)$$

For chloroform, trichlorethylene and methylenechloride a rapid drop in E_{br} is observed even after the first breakdowns. Under the action of ultra-violet radiation these liquids also decomposed easily. On the basis of this fact one might suggest that the decomposition of some number of molecules is caused by

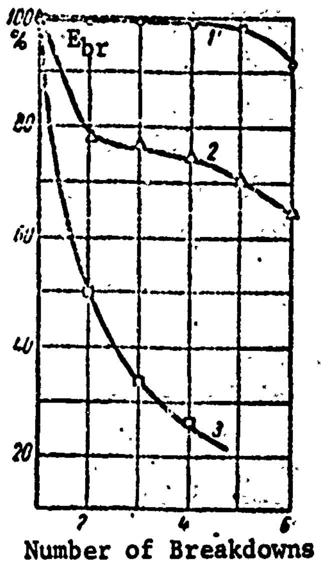


Fig. 8. Decrease in values of E_{br} for 6 breakdowns following one after another. 1-CCl_4; 2-$CHCl_3$; 3-CH_2Cl_2

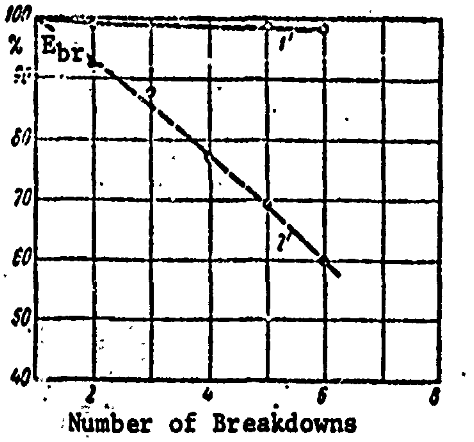


Fig. 9. Decrease in values of E_{br} for 6 breakdowns following one after another. 1-$(C_2H_5)_2O$; 2-$(CH_3CHO)_3$

the action of ultra-violet light radiated from the spark in the brakdown.

On a logarithmic scale the dependence between ε and E_{br} is expressed by a straight line (see Figure 10):

$$\log E_{пр} = -k\varepsilon + c, \tag{5}$$

where k and c are constants. They are determined from the equation of a straight line on the coordinates $\log E_{br}$ and ε. It is known that in this case k equals tgϕ, where ϕ is the slope angle between the straight line and the abcissa axis, and c is equal to the intercept, where the straight line intercepts the ordinate axis. From Figure 10

$$\log E_{пр} = -0{,}0588\varepsilon + 3{,}026. \tag{6}$$

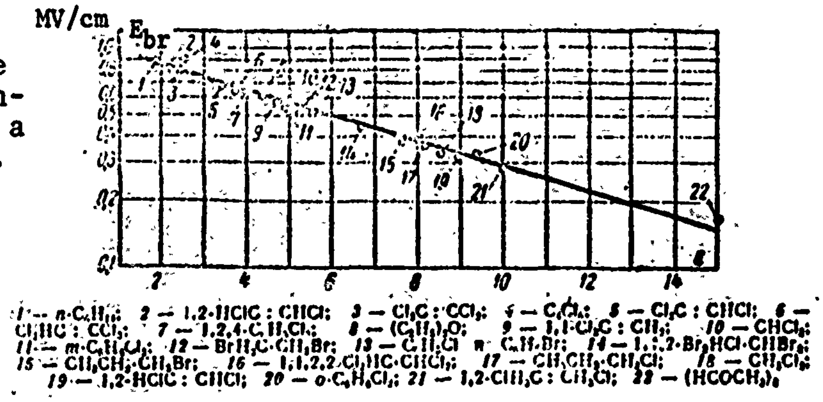


Fig. 10. Dependence of E_{br} of various insulating liquids on a dielectric constant.

It turned out feasible to extend such regularity to isomers, i.e., to liquids with the same chemical formula but with a different molecule structure. In Table 6, for instance, data on E_{br}, ε, and the dipole moments μ for three isomers of dichloroethylene and two isomers of dichlorobenzine are presented.

For the isomers of heptane with the same values of ε almost identical values of E_{br} were obtained:

	E_{br}, mv//cm	ε
N-heptane (C_7H_{16})...............	0.840	1,930
2,2-dimethylpentane (C_7H_{16})...	0,846	1,965

However, for spark gaps of several tens of microns for the same isomers, as was mentioned in the preceeding paragraph, a reverse relationship was found. Here, this was explained as an effect of the side molecule chains. Measurement of the values of breakdown voltages with DC and AC voltages in reference (L.34) could be made with an accuracy up to several percent, but the difference in values of E_{br} for the isomers compared was obtained with an accuracy of less than one percent. Therefore, there is still no sufficient justification for placing beyond doubt any conclusions drawn on the influence of side chains of liquid hydrocarbons on E_{br}.

Table 6

Values of E_{br}, ε and μ for Isomers of Dichloroethylene and Dichlorobenzine

Isomers	E_{br} MV/cm	ε	μ-10^{18} CGS Units
1.2-trans-dichloroethylene	0,815	2,18	0,00
1.1-dichloroethylene	0,506	4,82	1,18
1.2-cis-dichlorobenzine	0,317	8,92	1,80
M-dichlorobenzine	0,538	4,90	1,50
O-dichlorobenzine	0,312	9,43	2,27

For liquids with the dipole moments μ, with various values of ε the values of E_{br} turned out also to be very different:

	E_{br}, mv/cm	ε	$\mu \times 10^{18}$
Monochlorinebenzine (C_6H_5Cl).......	0.499	5.54	1.55
Methylenechloride (CH_2Cl_2).........	0.326	8.56	1.57

For N-hexane with inter-electrode distances of several tens of microns and with rectangular pulses with duration 0.25 microseconds, E_{br} equals 1.89 mv/cm (see Table 1). According to the data of reference (L.34) however, for variable and constant voltages and for wider spark gaps E_{br} equals 0.868 mv/cm for the same liquid (see Table 5).

The authors of references (L.34) are of the opinion that for short lengths of time over which the voltage is applied only polarization by virture of the shift of orbital electrons occurs. In this process an increase in ε is not produced, and consequently E_{br} also does change. But if there are constant dipoles in the liquid, then with an increase in voltage application time they will attempt to occupy a definite position along the field, i.e., an orientation mechanism will be brought into action. The dielectric will rise and E_{br} will fall. This is a very marked effect in the breakdown of a strongly polar liquid such as water (L.35).

One might add to what has been said that with an increase in ε the impurity molecules, as a result of the action of local fields, will more easily undergo dissociation and the work function of electrodes from the cathode will be reduced (L.36). Therefore the conditions for a cold emission from microscopic projections on the cathode will be more favorable. All of this taken together must facilitate the formation of breakdown for smaller values of E_{br}.

The data for E_{br} pertaining to cyclohexane and dibromoethane according to Table 5 also provide evidence for the absence of regularity in increase of E_{br} with an increase in d. The breakdown voltages for the liquids being prepared are equal respectively to 0.83 and 0.42 mv/cm and their densities are 0.7785 and 2.9638 g/cm^3.

For very small changes in ε (parts per hundred) a clearly expressed dependence of the type E_{br} equals $f(\varepsilon)$ apparently does not exist (see Table 3).

CHAPTER II

The Electric Strength of Mixtures and the Effect of Moisture and Absorbed Gases on E_{br} of Liquids

2-1. The breakdown voltage of mixtures of various liquids.

Experiments have shown that the breakdown voltage even of carefully purified and isolated liquids may be increased by the introduction of various admixtures. For instance a small addition of air into degassed transformer oil increases it E_{br} by approximately twenty percent (L.27). This same effect may be attained with the presence of a 0.01 gram per litre admixture of iodine (L.38).

Interesting data on the electric strength of mixtures were obtained in reference (L.39). These authors produced breakdowns with AC voltage at 50 hz. The distance between the spherical electrodes was between 1 and 1.75 mm. The discharged current was limited by ohmic resistors. The glass vessel was treated with potassium bichromate, was rinsed with distilled water and heated to 200°C, and before the measurements it was washed with the liquid to be studied. The electrodes were polished to a shine. The liquids to be studied were given multiple filterings and were twice distilled.

It was shown that the electic strength of a mixture of hexane and heptane with the same U_{br} does not depend upon the concentration of each of them. In the case of an addition of a polar liquid for which U_{br} is less than for the basic non-polar liquid, the breakdown voltage for small concentrations grows up to a certain limit and then, depending upon the degree this concentration is increased, it drops steeply. Such behavior in the variation of U_{br} is followed for heptane when chlorobenzine is added to it ($\varepsilon = 5.54$). The corresponding curve is presented in Figure 11, where along the axis of the abscissa the concentration of the indicated admixture is plotted in percent. The largest growth in U_{br} (by 40%) is observed with an addition of 8% chlorobenzine.

In Figure 12 curves for the variation of U_{br} for the same heptane but with different additives are presented. The maxima of U_{br} are attained for various content percentages. This information says something about the chemical nature of the additives. The chemical composition is also a quite significant factor. It is possible that the structure of the basic liquids to which the additives are applied is also important. For instance, this same chlorobenzine in the case of arbitrary additions within the limits of 1 to 100% does not cause any increase in U_{br} for xylene.

It turned out that the electric strength of transformer oil may be increased also with admixtures of nitrobenzine and chlorobenzine. We may obtain some hint about this from the curves of Figure 13. With the addition of chlorobenzine, U_{br} increases by about 11%.

Subsequently, as one might expect, other liquids will be found which as impurities give a more significant increase in U_{br}. But in this connection it is necessary to clear up some questions on the aging of transformer oil in prolonged use. The mechanism by which U_{br} is increased consists apparently of the capture of free electrons by impurity molecules. The formation of breakdown is slowed by this process.

On the increase of U_{br} for cable and petroleum ether with the introduction of various additives some information is reported in reference (L.40). An addition of 1% P-nitrotoluene

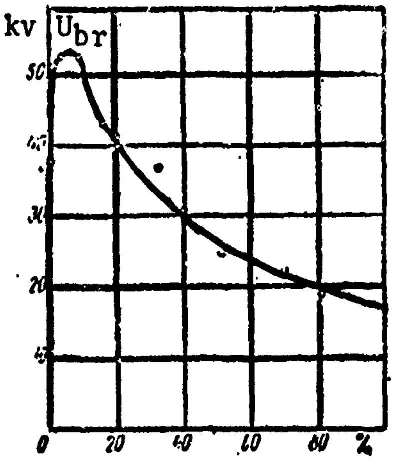


Fig. 11. Breakdown voltage of heptane as a function of chlorobenzine concentration.

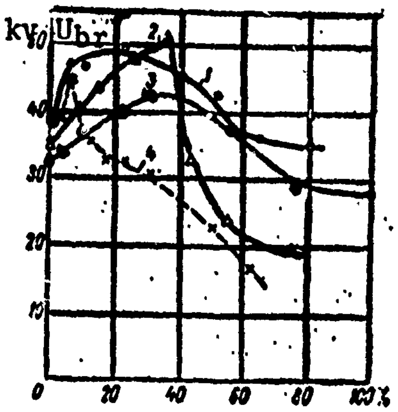


Fig. 12. Breakdown voltage of heptane as a function of various additions of other liquids. 1-quinone; 2-bromobenzine; 3-iodobenzine; 4-nitrobenzine

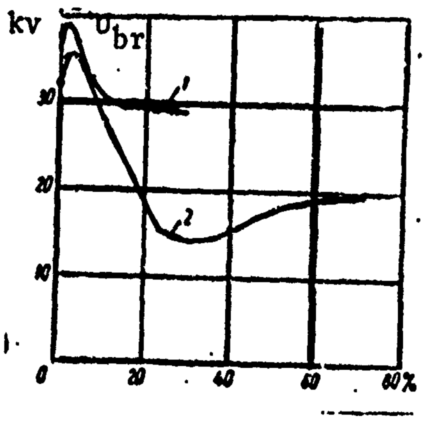


Fig. 13. Breakdown voltage of transformer oil with additions of other liquids. 1-nitrobenzine; 2-chlorobenzine

increases the breakdown of petroleum ether by 42%. For cable oil U_{br} rises by 48% as a result of an introduction of 2% 8-hydroxylquinoline.

It was proved experimentally that in the mixing of polar liquids the dependence $E_{br} = F(\varepsilon)$ is preserved, as was reported in Article 1-5. These liquids were investigated: methylene chloride (CH_2Cl_2), chloroform ($CHCl_3$) and trichlorethylene (Cl_2C: $CHCl$). Diethylether $(C_2H_5)_2O$ was added to them in various ratios. The change in E_{br} is shown by the curves in Figure 14, and the change in dielectric constant is shown in Figure 15 (L.34). The fractions x of additions of diethylether are plotted along the axis of the abcissa. With no addition ($x = 0$) the curves of Figure 14 indicate the values of E_{br} of the basic liquids (0.670; 0.545 and 0.325 mv/cm). For $x = 1$ the value of E_{br} equals 0.580 mv/cm refers to diethylether alone.

The breakdown of Cl_2:CHCl is equal to 0.67 mv/cm, and additions of $(C_2H_5)_2O$ is only 0.58 mv/cm. Therefore, with a growth in the fraction of $(C_2H_5)_2O$ the values of E_{br} of the mixture decrease. For (CH_2Cl_2), on the contrary, E_{br} is less than for $(C_2H_5)_2O$, and for an increase in the addition E_{br} of the mixture rises continuously. Curves for ε of the mixtures show a reverse relationship. The larger the admixture of $(C_2H_5)_2O$ in CH_2Cl_2 the smaller ε is, and so forth (L.34).

In Figure 15 for $x = 0$ the values of ε are indicated for some liquids without additives (8.56; 4.89 and 3.44). For $x = 1$ at the point of convergence of the curves ε of diethylether is equal to 4.38.

In the case of mixing of weakly polar and non-polar liquids the situation is apparently somewhat different. From the curve for a mixture of transformer oil and chlorobenzine

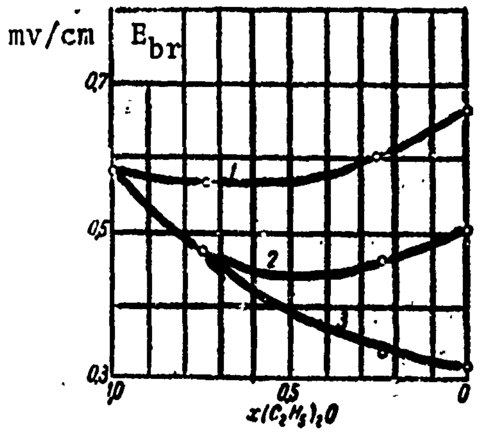


Fig. 14. Values of E_{br} of various liquids in mixture with diethylether. 1-trichlorethylene; 2-chloroform; 3-methylenechloride

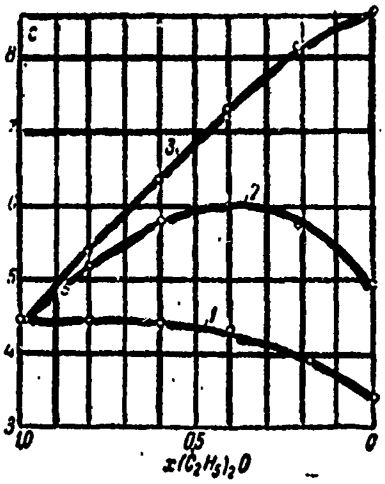


Fig. 15. Values of the dielectric constant of mixtures with diethylether. 1-trichlorethylene; 2-chloroform; 3-methylenechloride

in Figure 13 it is apparent that there are two extremum points. For an addition of 30% chlorobenzine, a minimum in E_{br} appears. Therefore, the general rule, according to which the breakdown voltage decreases with a rise in ε, is not applicable in the given case.

In reference (L.41) a carefully purified and thoroughly degassed sample of N-hexane was studied. Its breakdown voltage was equal to 0.89 mv/cm. Admixtures of nitrogen did not change this voltage, but an addition of oxygen caused it to rise to 1.3 mv/cm.

For liquid argon when oxygen was added E_{br} also rose. The corresponding experimental data have been collected in Table 7. They were obtained with direct-current voltage and with l equal to from 2 times 10^{-3} to 10^{-2} cm (L.42 and 43).

From the Table, it is clear that an addition of 20% oxygen increases E_{br} of liquid argon by approximately a factor of two in the case of an aluminum anode; and for a steel anode by 60%. An explanation for the mechanism of this phenomenon will be presented in Article 4-3.

Table 7

Breakdown voltage for a mixture of liquid argon and oxygen with electrodes (spheres) of aluminum and stainless steel.

Liquid	Breakdown voltage, mv/cm	
	Anode of Aluminum	Anode of Stainless Steel
Technical liquid argon + 20% oxygen	1.350	1.710
The same + 1% oxygen	1.330	1.680
The same + 0.002% oxygen	0.686	1.070
Spectroscopically pure liquid argon + 0.002% oxygen	0.761	0.888

Here we may make mention of the capability of liquid chlorodiphenyls to form compounds with polar organic crystals which have a relatively small ε. Some mixtures which are formed in the solution of such crystals have a higher ε than the components which make up the solution. For example, a mixture of 75% pentachlorodiphenyl and 25% 2,4-dinitrodiphenyl has an ε of 15.8, and for 50% ε of the mixture increases to 25.4. Mixtures of pentachlorodiphenyl with O-nitrodiphenyl and α-nitronaphthaline yield heightened values of ε. However, the interaction forces between charged particles decrease by a factor given by ε; therefore, dissociation of the molecules occurs and the electrical properties are degraded (L.49).

2-2 The Effect of Moisture and Mixtures on E_{br} of Liquids

Even a small content of water in insulating liquids causes a noticeable drop in the value of E_{br}. For transformer oil we may get an idea of this from the curves of Figure 16, obtained by various investigators with direct-current and alternating-current voltages. It turned out that in order to obtain a sharp drop in E_{br} it was sufficient to have moisture content in the area of only hundredths of a percent. Further humidification, however, produces no noticeable effect on E_{br} (L.44).

In the preceeding paragraph data were presented on the temperature dependence of E_{br} of various liquid dielectrics and a hypothesis was stated regarding the possible influence of processing methods and of impurities on the trend of the curves of $E_{br} = f(T)$. To serve as an illustration of this in Figure 17 the temperature dependences of E_{br} for transformer oil are presented with a varying content of moisture (L.45). With an increase in moisture E_{br}, as always, decreased, but the appearance of a temperature maximum in E_{br} at T about equal to 65°C may be considered typical. It is a curious fact that in the cooling of the oil the curve again passed through a maximum. The addition of water made this maximum sharper and more prominent.

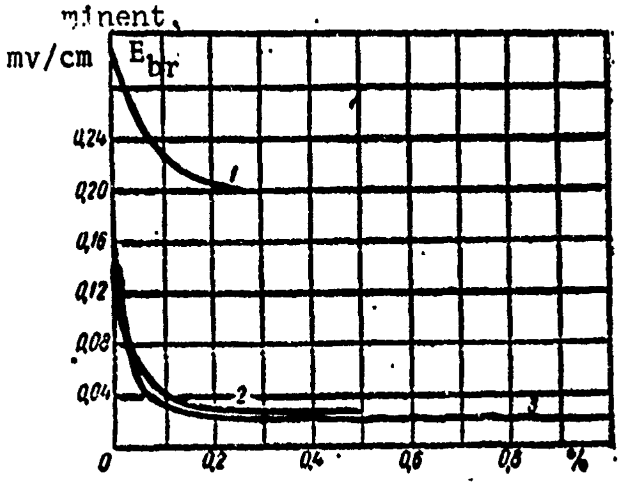


Fig. 16. The effect of moisture on E_{br} of transformer oil. 1-according to Snats; 2- according to Peak; 3-according to Frieze

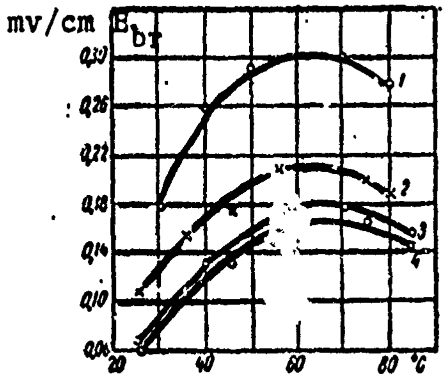


Fig. 17. The dependence of E_{br} of transformer oil on temperature for varying content of water C. 1-C less than 0.002%;2-C = 0.001%;3 = 0.005%; 4-C = 0.1%

Minerals may contain water in three different forms (L.46): 1) in a dissolved state; 2) in the form of an emulsion, i.e., droplets with diameter of about 10 microns, and 3) in the form of a sediment on the bottom of the vessel with oil (coarse drops). With heating of the oil the water from the sediment may go into the first or second form. Apparently transitions are possible from the second form into the first. It was revealed that in such transitions the breakdown changes noticeably. The dissolved water has almost no effect on E_{br} (L.45), and in the emulsified form it causes this quanity to fall, One may surmise that the curves in Figure 16 were recorded when the water was contained in the form of an emulsion.

In proportion with the rise in temperature and the transition of the water from an emulsified state to the dissolved state, E_{br} will increase until other factors, lowering this quantity, for instance gas bubbles, begin to manifest themselve. Gases may also exist in insulating liquids in the dissolved and emulsified states (see L.47).

In nonpolar liquids such as transformer oil, benzine, hexane etc., saturation by aqueous solution at room temperature is expressed in hundredths of a percent. When surface-active substances (organic acids) are present in liquids the conditions are created for a large solubility of water on account of the formation of emulsions. Thus in liquids with admixtures of polar surface-active substances there always exist water emulsions. The amount of water in molecular-solution form, when increasing the temperature, initially drops to a certain minimum, and then it begins to grow. In the purification of transformer oil with concentrated H_2SO_4 usually some amount or other of the aromatic phase is removed and consequently also the surface-active substances. This situation alters the content of water emulsion exerts an influence on E_{br}.

Thus the breakdown voltage will be determined both by the overall content of the water in the insulating liquids and by its distribution coefficient between the molecular and the emulsion form (L.48).

The appearance of a temperature maximum of E_{br} of transformer oil with the specified content of moisture may be explained by a change in this coefficient. For thoroughly dehydrated oil, E_{br} does not rise with an increase in temperature.

The temperature maximum of E_{br} is observed also in certain other liquid dielectrics with impurities. In Figure 18, for instance, a curve for the dependence of $E_{br} = f(T)$ for xylene is presented. An addition of 0.25% water and 0.2% naphthenic acid is made to the liquid. The maxima of E_{br} are easily discernible at 50 and 45°C respectively.

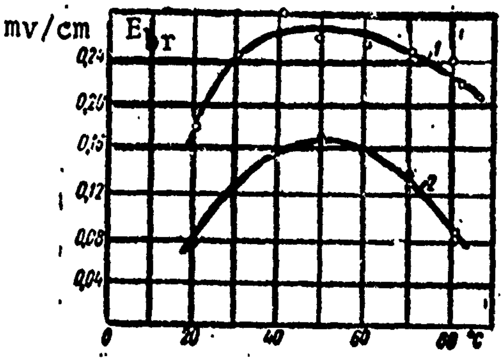


Fig. 18. The breakdown voltage of xylene with admixtures at various temperatures. 1-AC voltage; 2-DC voltage

If humidification, various types of gas saturation and contamination as a rule degrade the electrical properties of liquid dielectrics it follows that drying, degassing and filtering act essentially in the reverse direction. The effect of various methods of purification may be shown in an example for silico organic liquids. They were dried in the presence of metallic sodium and filtered through glass filters. Suspended particles of a diameter greater than 10^3 mm were thereby retained. In order to remove dissolved gas, distillation. The measuring vessel was made of glass and the electrodes were also carefully cleaned. The gap between the electrodes broke down at $l = 8 \times 10^{-3}$ mm. with DC voltage (L.27).

The experimental data obtained are reported in Table 8.

Table 8

The effect of purification and degassing on the breakdown voltage silicoorganic liquids

Method of purification	Breakdown voltage with DC mv/cm			
	dimer	trimer	tetramer	pentamer
Distillation and filtration	0.93	0.98	1.04	1.100
Distillation, filtration, and degassing	0.96	1.00	1.11	1.160
Drying, distillation, filtration and degassing..	0.98	1.03	1.14	0.117

In connection of the question of impurities in oils mention should be made also of the silico organic mixture of domestic manufacture (kaloriya-2) with ε about equal to 2.5 and E_{br} about equal to 0.3 mv/cm (L.49). It is a mixture of products with different molecule chain lengths. Therefore it boils at a relatively low temperature. At 150°C the low boiling fractions have already begun to come off. This situation detracts from the quality of the products and limits its applicability (L.50).

At the present time in the Soviet Union new silico organic compounds have been developed -- bistrialkylsiloxanebenzenes (L.50, 51, and 52). They differ from the kaloriya-2 in the position of side chains. Some of the electrical properties are enumerated below:

Molecular weight	366-506
Boiling temperature at 760 mmHg	330-400°C
Melting temperature	below -60°C
Flash temperature	185-215°C
Density at 20°C	0.90-0.92
Viscosity at 20°C	from 6 to 36 centistokes
Dielectric constant	3-4
Dielectric loss tangent angle at 50 hz	from 8 to 13 x 10^{-4}

For AC voltage and for l about equal to 2 mm the breakdown voltage of unpurified and undegassed liquids amounts to about 0.15 mv/cm. There is no doubt but that the corresponding purification allows their electric strength to be increased significantly. The presence of side chains however, as was shown in Article 1-4 and 1-5, reduces somewhat the value of such products. Evidently the silicofluoroorganic liquid dielectrics have the greatest prospects (L.53).

Fluoroorganic liquids are generally slightly hydroscopic. But even with an insignificant amount of moisture their electrical properties deteriorate drastically (L.49). We may get an idea of this from the data of Table 9.

The breakdown voltage for a specified gap between electrodes may be lowered by more than a factor of 2 with humidity, and the resistivity may be lowered by a factor of 3 or 4.

Experiments showed that suspended matter of various types significantly degrades the electric strength of liquid dielectrics. It is clear from the example with xylene which was not thoroughly purified. For DC voltage and for $l = 0.4$mm its breakdown voltage was equal to 3-7.5 kv. However after a filtration through a pot of unfired clay U_{br} increased to 27.6 kv (L.54).

Table 9

The effect of moisture on breakdown voltage and resistance of flouroorganic liquids

Chemical Composition of Liquids	U_{br} in the dry condition KV	U_{br} after storing in an atmosphere of 90% relative humidity KV		RHO in the dry condition, OHM CV	HO after storing in an atmosphere of 90% relative humidity OHM CM	
		After period of 10 days	After period of 80 days		After period of 10 days	After period of 80 days
$c\text{-}C_8F_{16}O$	40	17	17	10^{15}	$5\cdot10^{13}$	—
$(C_6F_{13})_2O$	40	15	17	10^{15}	$2\cdot10^{12}$	$3\cdot10^{11}$
$(C_4F_9)_3N$	40	15	—	10^{15}	$4\cdot10^{13}$	—

We may supplement the above paragraph somewhat with a report on the electric strength of insulating liquids containing metallic powder. If the particles of diameter 4 to 40 microns are added to benzine, vaseline oil or ethyl ether then for a DC voltage between the electrodes bridges are formed whose resistance remains relatively high. Such bridges of particles of copper with diameter of about 40 microns in benzine have a resistance of about 25 ohm (L.55). But the breakdown voltage of the indicated liquids containing metal dust is approximately the same (about 4 kv/cm).

In carrying out the indicated experiments it was noted that the suspended particles were in rapid motion in the direction toward the cathode. The dielectric constant of metallic particles, as is well known, is quite large, and according to the Cohen rule they must carry a positive charge.

2-3. The Role of Dissolved Gasses and External Pressure.

In Article 1-3 the statement was made that as far as the gaseous state was concerned liquids act as if they were compressed under a pressure roughly equal to 2000 atmospheres. Therefore under the action of external pressure amounting to several tens of atmospheres they compress practically not at all. Their density remains the same and there is no reason for any of their parameters to change. The breakdown voltage under such circumstances would not have to change if the liquids did not contain any dissolved gasses which under the application of a voltage have a tendency to accumulate into small bubbles. It was noted that this process depends on the external air pressure above the liquid.

The mechanism of bubble formation is not completely clear. It is not known whether they originate directly from the molecular-dissolved gas or whether the latter converts first of all into an emulsified state; finally, coagulation processes are also possible in the presence of emulsions. According to the data of reference (L.56), the curves of the dependence of $E_{br} = f(p)$ for liquids saturated with air at atmospheric pressure do not differ greatly from the same curves for liquids containing no more than a few percent of the amount of air which they adsorb upon saturation. The conclusion drawn from this is that the bubbles do not form from the gas dissolved in the liquid as was assumed in reference (L.57 and 58). Experiments showed further that E_{br} of liquids depends on the external pressure even when the cathode is in the form of a point. Inasmuch as the service of the electrode in this case is very small, the conclusion was drawn to the effect that the bubbles do not from from the gas adsorbed on the surface of the cathode, as was confirmed in reference (L.59-61).

In Figure 19 a series of curves of the dependence of E_{br} on pressure -- above and below atmospheric pressure -- for various liquids is presented (L.62, 63, and 64).

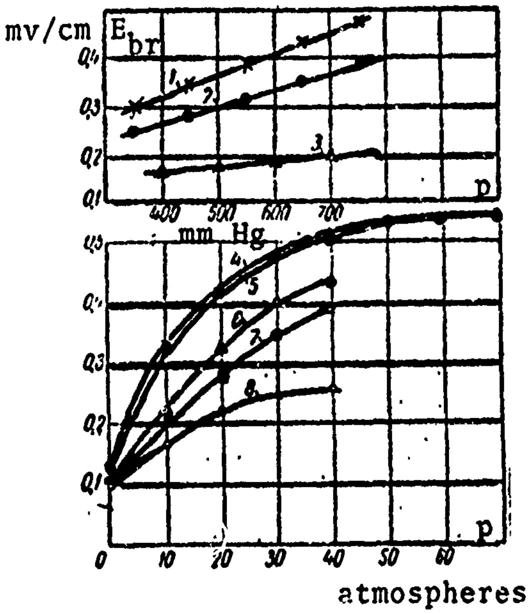


Fig.19. The dependence of E_{br} of insulating liquids for DC and AC voltages as a function of external pressure. The upper curves were obtained for pressures below atmospheric and the lower curves for the pressures above atmospheric. 1-xylene; 2-hexane; 3-transformer oil; 4-petroleum; 5-castor oil; 6-transformer oil with AC voltage at 50 hz; 7-the same but with AC voltage at 20 hz; 8-the same but with DC voltage.

At pressures below atmospheric the dependence $E_{br} = f(P)$ is linear:

$$E_{br} = A + BP, \tag{7}$$

where A and B are constants. Numerical values of A and B for some liquids are given in Table 10.

According to the data of reference (L.64) for some unpurified liquids E_{br} rises relatively steeply up to a pressure of 50 atmospheres (gauge). After that a slowdown in the growth of E_{br} an finally and end to its growth at P greater than

70 atmospheres (gauge) is observed, for instance for petroleum and transformer oil. For DC voltage (curve 8 in Fig. 19) this growth turned out smaller than for AC voltage (curves 6 and 7).

Table 10

Numerical values of the constants A and B in the formula (7) for certain liquids

Liquids	A/mv/cm	B/mv/cm A/M gauge
Transformer Oil	0.122	0.080
Xylene	0.159	0.230
Hexane	0.144	0.320

Undoubtedly the degree of degassing of the liquids and the duration of voltage application must exert a significant effect on the size of E_{br} under the indicated conditions. At a temperature close to the boiling point the separation of gasses is intensified and E_{br} drops sharply. This is illustrated very well by the curves $E_{br} = f(P)$ in Figure 20. They are recorded in experiments with xylene. Breakdown occurred with a gap of several tenths of a millimeter with DC voltage. The temperature varied within the limits from 16 to 145°C (L.65). The dotted lines in Figure 20 indicated the boiling point of xylene for the given pressure above the liquid.

Inasmuch as a certain time is required for formation of gas bubbles and the formation therein of the shock ionization process, the dependence of E_{br} on the pressure above the liquid would have to be determined in some degree by the duration of application of voltage. In the literature of former years one may find statements to the effect that E_{br} of many liquids sub-

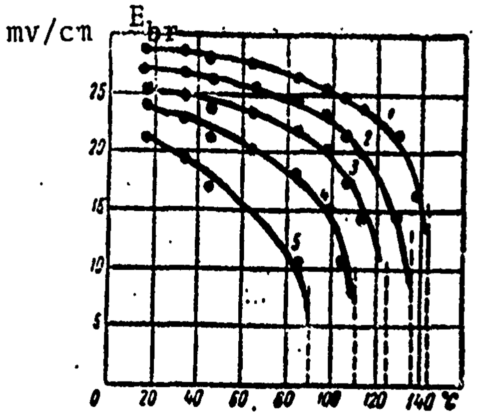


Fig. 20. Breakdown voltages of xylene for various temperatures and pressures (P). 1-P = 750 mmHg; 2-P = 600 mmHg; 3-P = 450 mmHg; 4-P = 300 mmHg; 5-P = 150 mmHg.

jected to voltage pulses (aperiodic pulses) does not depend on the external pressure (L.65). This fact is established in experiments with xylene (l = 0.5 and 0.8 mm), transformer oil (l = 0.5 mm) and hexane. This kind of regularity was established with temperatures greater than and less than atmospheric.

It is necessary to observe that aperiodic pulses, especially with a steep front and sharp drop in amplitude, are not altogether convenient for investigations of this type. Liquids especially break down with a definite delay interval. For instance, according to the data of reference (L.56), this delay time for liquid hydrocarbons of the paraffin series equals 1 microsecond for I = 33 microns, and amounts to 3.5 microseconds for l = 200 microns. In the investigation of xylene and transformer oil (L.65) gaps of 0.5 to 0.8 mm experienced breakdown and the delay time could equal as much as several microseconds. If these were realized with steep aperiodic pulses, then E_{br} could not really depend on pressure, but only by reason of a comparatively delay time in the breakdown.

In experiments with square pulses (L.56) it was shown that E_{br} of many liquids rises with an increase in external pressure. The corresponding curves are presented in Figure 21. They were recorded with square pulses of duration of 4.5 microseconds. Breakdown was produced in a gap with l = 200 microns between hemispherical electrodes of stainless steel with

D about equal to 6 mm.

It is seen from Figure 21 that the degree to which E_{br} rises with an increase in pressure depends on the chemical nature of the liquids. Apparently a basic role is played in this process by the capacity of the liquids to liberate and to adsorb gas, and also by the condition for formation of bubbles at the moment that the voltage is applied.

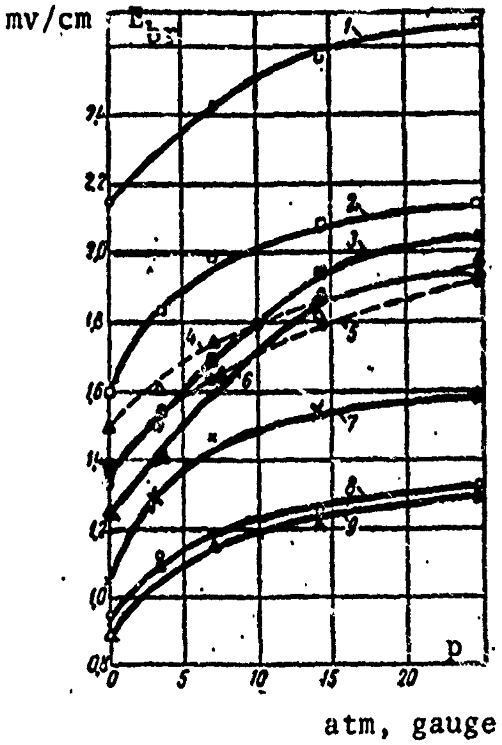


Fig. 21. The dependence of E_{br} of degassed liquids on external pressure. 1-hydrocarbon substituted with four chlorines; 2-N-decane; 3-toluene; 4-N-heptane; 5-N-hexane; 6-benzine; 7-chlorobenzine; 8-ethyl alcohol; 9-methyl alcohol

The same sort of dependence of E_{br} on external pressure is found also with square N-hexane subjected to square pulses of other durations lying in the range from 1 to 1000 microseconds (see Figure 22). The shape, electrode material and distance between them were the same as in the curves recorded in Figure 21.

The statements above however, do not constitute an exhaustive treatment of the dependence of $E_{br} = f(P)$ by any means. There are indications, for instance, that the increase in E_{br} with a rise in pressure is connected with the emulsified state of a gas in the liquid (L.47).

Experiments of this sort were performed with DC voltage using toluene twice distilled under vacuum. Electrodes of stainless steel had the shape of hemispheres. Above the surface of the degassed toluene the pressure varied from 50 to 350 mmHg. The breakdown voltage of the liquid in this case did not change. The same was observed also after the toluene, passing through a U-shaped tube containing calcium chloride and phosphate anhydride , was saturated with dry air, but in such a way that the gas existed in the molecular-dissolved state.

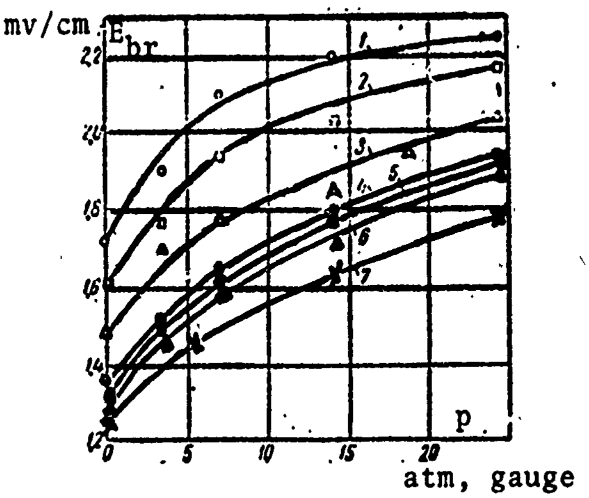


Fig. 22. Dependence of E_{br} of degassed N-hexane on pressure with pulses of varying duration τ 1-τ = 1 microsecond; 2-τ = 1.5 microseconds; 3-τ = 2 microseconds; 4 - τ = 4.5 microseconds; 5-τ = 10 microseconds; 6-τ = 28 microseconds; 7-τ = 1000 microseconds.

The following series of experiments with the same degassed toluene was carried out in such a way that after saturation of the liquid under study with air it was shaken over an interval of thirty minutes until the emulsified gas appeared. As a result of this E_{br} of the toluene dropped significantly.

Quite interesting data were obtained in experiments with oil for filling cables (L.66). At 20°C they all had a viscosity of 25 centistokes. The dry air pressure above the surface of the oil varied from 5×10^{-6} to 1000 mmHg. With DC voltage breakdown occurred in a gap with $l = 0.5$ mm between platinum electrodes. The breakdowns were experienced only after full equilibrium had been attained for the gas dissolved in the oil with free gas above the surface. If the oil had previously been saturated with dry air at a pressure greater than that above the surface, its E_{br} was significantly lowered. In order to attain equilibrium the liquid was held over a period of 24 hours at the given temperature and pressure. Only after this step were the measurements of E_{br} made with ten different tests of the oil. In this case the gas evolved in the breakdown did not destroy equilibrium. It turned out that the breakdown of the oil, equal to 0.4 mv/cm, under such conditions did not depend on external pressure.

The authors of reference (L.66) are of the opinion that ions or charged suspensions in motion along the field separate the oil particles as if by pushing them apart and form cavities in which the gas accumulates. With field strength sufficient for ionization of the gas in these cavities breakdown of the liquid occurs.

Apparently with a given pressure the liquid can adsorb completely a definite quantity. With a reduction in pressure the adsorbed gas is liberated. It is possible that this process facilitates the dissolution of gas into microscopic bubbles.

From the curves of Figure 21 and 22 it is seen that even for degassed liquids E_{br} depends upon external pressure. This dependence assumes that gas is present in the liquids and that it plays a role in the formation of breakdown. But what is the source of this gas which appears in degassed liquids? In order to find an answer to this question experiments were set up and performed, and the details have been reported in references (L.67 and 68). The experiments were conducted with colorless, well-purified and degassed mineral oil. The evolution of gas at the moment that the field was imposed was recorded by a manometer installed over the surface of the liquid.

The experimental curve of gas evolution from the liquid corresponding to various E is presented in Figure 23. Here the pressure in the manometer is plotted along the ordinate axis and the time in hours is plotted along the axis of abscissas. With an increase in E the amount of gas liberated rose.

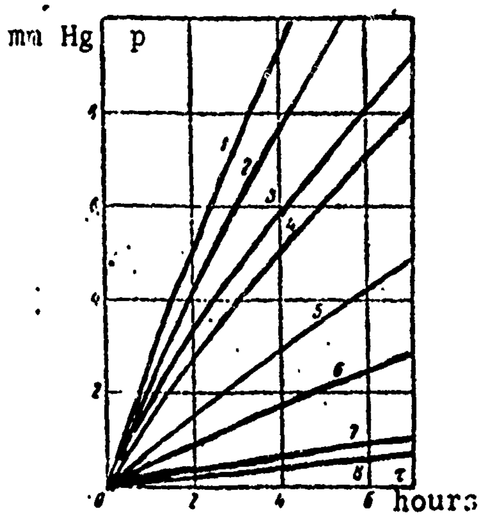


Fig. 23. Intensity of gas liberation from mineral oil as a function of time for various voltages. 1-11 kv (0.151 mv/cm); 2- 10 kv (0.138 mv/cm); 3-9kv (0.125 mv/cm); 4-8 kv (0.110 mv/cm); 5-7 kv (0.097 mv/cm); 6-6 kv (0.083 mv/cm); 7-5 kv (0.069 mv/cm); 8-4 kv (0.055 mv/cm).

The following empirical expression was found for the rate of gas liberation: dP/dτ (L.67):

$$\frac{dP}{d\tau} = k(U - U_s)^n P^k \text{ [мм рт. ст./час]}, \quad (8)$$

where U is the applied voltage in kv; U_s is the voltage in kv at which gas evolution begins; k is a constant; and P is the gas phase pressure in mmHg.

For voltages below 40 kv/cm gas evolution is not observed. The authors of reference (L.67) connect the process of gas evolution with the destruction of molecules of liquid by cold emission electrons from the cathode and they believe that the latter becomes significant at a voltage of 40 kv.

According to the data of reference (L.68), the rate of gas liberation from transformer oil is a linear function of voltage. Evolution of gas ceased at E = from 12 to 16 kv/cm.

Apparently the indicated process is determined by the degree of purification of the oil and by the chemical composition of the petroleum from which it is obtained. Cessation of gas evolution may be attained not only by a lowering of the voltage, but also by an increase in the pressure above the liquid. This situation would also seem to confirm the hypothesis which states that the gas dissolved in the liquid or formed as a result of disintegration of molecules stimulates the formation of bubbles when it comes out to the surface. When the pressure is increased fewer such bubbles are formed and E_{br} of the liquid increases, but there does not exist as yet a clear understanding with respect to this question.

It is worthwhile to mention that in addition to the external pressure the liquid is subjected to an internal pressure (P) at every point of the field when a voltage is applied. A mathematical expression for the size of this pressure had been given already in 1881 by Helmholtz:

$$\Delta P = E^2 \frac{(\varepsilon - 1)(\varepsilon + 2)}{24\pi}.$$

The validity of this formula was confirmed not long ago in reference (L.69) by measuring the index of refraction in carbon tetrachloride and in N-hexane. Gaps of several hundredths of microns were studied with E = 0.5 mv/cm. Meanwhile there has been no information in the effect of this pressure on the formation of gas bubbles in the insulating liquids.

2-4. The Effect of Electrical Conductivity on E_{br}

Usually it is considered that the principal source of charged particles in highly purified and non-polar liquid dielectrics is external ionizing radiation. According to the data of reference (L.70), conductivity in N-hexane may be lowered by several orders of magnitude if the measuring vessel is placed into a lead housing with a wall thickness of 6 cm. But the effect of ionizing radiation may not be noticed if the charged particles which have been formed recombine rapidly and if in order to separate them it is necessary to apply a relatively large field intensity (L.71 and 72), as for instance in liquid oxygen or isooctane.

The source of the current carrier may also be colloidal particles of moisture and other impurities, and for large voltages also cold emission of electrons from the cathode and even weakly bound ion complexes (L.73). Moreover, there is some evidence that for even higher field intensities, close to breakdown intensities, electron conductivity occurs in some cases (L.74), but there is no more detailed information on this at the present time.

It is well known that in the case of a significant increase in electrical conductivity for insulating liquids their breakdown voltage falls. This is most noticeable for DC voltage. Very pure liquids , for instance N-hexane, have a σ of about 10^{-19} ohm^{-1} cm^{-1}. The breakdown of this compound is also quite considerable. The question arises as to what influence the initial electrical conductivity of the liquids has on their breakdown voltage. It would seem that the greater σ is the smaller E_{br} would have to be. If we turn to the analogy of breakdown in gases then according to the classical theory of Townsend the current across the gap between electrodes may be expressed with the following formula:

$$J = J_0 \frac{(\alpha-\beta)e^{(\alpha-\beta)l}}{(1+\gamma)\alpha-(\alpha\gamma+\beta)e^{(\alpha-\beta)l}}, \tag{9}$$

where α, β, γ are ionization coefficients, and J_0 is the initial current. With a decrease in the denominator, when $(1+\gamma)\alpha$ $(\alpha\gamma+\beta)e^{(\alpha-\beta)l}$, J must rise to breakdown, and this may occur if at the local position the liquid begins to boil. The initial current J_0 also may be considered one of the parameters which determine the formation of breakdown. For small values of l and for DC voltage, when the emission of electrons has begun to play a positive role, the initial conductivity must facilitate the grouping of positive ions on the oxide surface of the cathode, and consequently must reinforce the emission of electrons.

However, it was noted long ago that the U_{br} of purified xylene does not change following a significant raising of its σ by the addition of aniline (L.54). No dependence of E_{br} on the electrical conductivity of liquids is detected nor is it for some types of mineral oils.(L.75). The same situation is observed in other references.(L.76,77-80).

From the statements made above one may come to the conclusion that at least for some liquids a comparatively small increase in electrical conductivity does not exert an effect on E_{br} even with DC voltage.

But in individual cases the opposite relationship holds: with a rise in σ E_{br} also increases. This is found in an investigation of distilled water and certain aqueous solutions. Breakdowns occurred with a pulsed voltage. In order to increase the conductivity solutions of NH_4OH, BACl, NACl, NAOH and HCl were added to the water. Some of the data obtained are presented in Table 11 (L.81).

Table 11

Breakdown voltage of water and aqueous solution

Object of Study	Width of spark gap mm	Electrical conductivity OHM-1 cm	Breakdown voltage KV
NH_4OH (0.05N) (Aqueous solution)	0.4	$10.5 \cdot 10^{-4}$	25
The same	2.0	$10.5 \cdot 10^{-4}$	28
Distilled water	0.4	$1.43 \cdot 10^{-4}$	18
The Same	2.0	$1.43 \cdot 10^{-4}$	35

From this table it is seen that the ionic electrical conductivity σ of an aqueous solution of NH_4OH is almost seven times greater than for distilled water. But its breakdown for $l = 0.4$ mm is not only not smaller, but is even greater than for water.

In the following chapter (see Article 3-4) it will be shown that for short pulses and small spark gaps the electrical conductivity of liquids also does not have an effect on their E_{br}. This has been established for the breakdown of distilled water (L.35) and of transformer oil (L.82).

The dependence of E_{br} on σ for short pulses may be connected with the decay time of ions in liquids, but it is very difficult to explain the increase in E_{br} for breakdown in aqueous solutions of NH_4OH. Inasmuch as the breakdown was experienced in comparatively large spark gaps, the formation of breakdowns must have proceeded with the significant participation of shock ionization.

The thermal form of breakdown with pulsed voltage is of low probability. If positive ions of the NH_4OH solution captured on a large scale the electrons of the avalanche which was forming, the breakdown voltage would actually be able to increase. For inter-electrode distances of 0.4 to

2 mm the material of the electrodes does not need to exert a noticeable influence (L.99), and consequently, in order to explain the growth in E_{br} it is hardly fitting to infer processes involving electrons.

In regard to a small inter-electrode distance (tens of microns) for DC voltage the small influence of σ on E_{br} may be readily explained by the change in conditions pertaining to the electrons. When positive ions accumulate at the oxide coating of the cathode, an equilibrium condition is apparently established. The positive space charge at this electrode reinforces the emission of electrons, which together with the positive ions will cause more serious damage to the coating and will reduce the extent of the emitting surface. Therefore a not-too-considerable change in σ will have a substantial effect neither on the emission of electrons, nor consequently on E_{br}.

It is necessary however to mention that the role of electrical conductivity in the mechanism of forming breakdown in liquids with DC voltage is still unclear in many respects.

CHAPTER 3

The Effect of Statistical Factors, Electrode Geometry and Voltage Application Time On the Electrical Strength of Liquids

3-1. The Spread of Experimental Values of U_{br}

It is well known that in the case where breakdowns are repeated within the same liquid under fixed conditions the values of U_{br} are somewhat different. This is a consequence both of unavoidable errors in the measurements and of different developments of the process of forming breakdown with respect to the action of various influencing factors. Moreover, with the high temperature of the spark thermal decomposition of the liquid occurs and in some cases the carbon is reduced.

Experiments have shown that the spread of values of U_{br} for liquid dielectrics under specified conditions may be significant. But in a uniform field the dielectric may still be characterized by an average value of the breakdown voltage. The argument here may be based on the curve in Fig. 24, which was constructed from the values of almost 500 separate mesurements of U_{br} in various tests of technically pure transformer oil. The maximum and minimum values of U_{br} were summed and divided by the number of breakdowns. The transformer oil was heated prior to the experiments in order to remove moisture and it was also filtered. The electrodes were molybdenum spheres of $d = 1$ *cm*, so that their surface was not heavily damaged with the thermal action of electrical sparks. Breakdown was produced with gaps of $l = 2$ *mm*. For the experiments a large quantity of oil was collected for each test in order that the decomposition product from the breakdowns would not have a strong effect on the results of the measurements. The electrodes were periodically rubbed clean of carbon black immediately below the oil. Thus, although the experiments were conducted under conditions far from ideal, it still appears to be true that one may characterize a technically

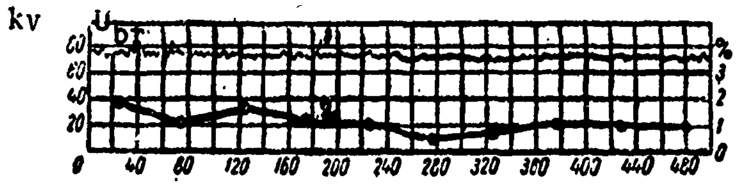


Fig. 24. Dependence of breakdown voltage (1) and percent deviation from the average breakdown voltage (2) as a function of the number of breakdowns.

pure insulating liquid by some average value of U_{br} (L. 83). Such experiments were carried out with other liquids as well. Based on the data obtained an empirical formula was proposed for the number of breakdowns N with an average deviation X from the average value of U_{br}:

$$N = ae^{-b(x-c)^2}$$

where a, b and c are constants which must characterize the individual insulating liquids.

The spread of values of U_{br} depends on the degree of purity of the liquids, as one might argue on the basis of the data from Table 12 (L. 84 & 85).

Apparently, a large role in this is played also by the chemical nature of the dielectric. For example, with technical and chemically pure benzene the difference in the spread of U_{br} is very small. The influence of the gap width between electrodes was also established. For greater width the spread turned out to be greater.

For the case of very carefully degassed electrodes in experiments with well purified N-hexane certain regularities in the changes of the value of U_{br} are observed. The experiments were performed in a uniform field and with DC voltage . The spark gap width between chrome plated spheres with $d = 13$ mm was equal to 0.25 mm. The discharge current was limited by an 18 megohm ohmic resistor. After breakdown had gone to completion the voltage from the spark gap was recorded by shunting with the aid of a thyratron.

Table 12. Spread in the Values of Breakdown Voltage for Some Liquid Dielectrics Purified by Various Methods

Dielectric	Degree of Purification	No. of Breakdowns	Spread in U_{br} values, %	Average U_{br} Value, Mv.
Transformer Oil	Technical	66	from 30 to 50	0.22
same	treated with centrifuge	66	from 5 to 10	0.31
Benzene	Technical	50	±14	
same	Chemically Pure	50	±12	
Air		50	±4	

Forty breakdowns were produced in one portion of N-hexane. After the first ten breakdowns the value of U_{br} increased. This increase depended on the electrode material. More or less stable values of U_{br} were observed only after 30 to 40 breakdowns. If the electrodes were thoroughly degassed, this increase in U_{br} was not observed.

Analogous data were obtained in the breakdown of dried and degassed transformer oil with short pulses and electrodes made from brass spheres with a gap of 2.5 mm. The reduction began only after 10 breakdowns (L. 86 & 87). For not too pure liquids the increase in value of U_{br} when the breakdowns were repeated may be considerable (L. 82).

From these statements one may conclude that the spread in values of U_{br} is determined by many factors. If the discharge current is severely limited but the electrodes not degassed, then in the first breakdowns no drop in U_{br} will have occurred from the thermal decomposition of the liquid, and the electrodes are to some degree degassed.

In what way should we characterize liquids in respect to their purity? Frequently we use the expression "technically pure liquids". Normally this signifies that the liquid has been purified chemically, and has been dried and filtered to such an extent that technological conditions are satisfied. Sometimes the liquids are purified by an electrical method. In this case charged particles at the electrodes are neutralized. However, when there is a significant difference in the dielectric constants of these particles and of the medium they may again acquire a charge (L. 88).

In order to obtain very pure liquids, it is necessary, in addition to chemical treatment, filtration and thorough drying, to remove the gases disolved in them also, for instance, by heating under a vacuum. Good results are gotten from distillation and filtration through glass filters with subsequent dehumidification with suitable moisture absorbers (calcium chloride, phosphate anhydride, metallic sodium, etc.). These operations are usually conducted in clean, glass vessels dried under vacuum at an elevated temperature. All unions and stopcocks must be used without grease, in order to protect the liquid from contaminants.

3-2. Breakdown Voltages for Various Interelectrode Distances and the Influence of the Area of These Electrodes

Over the last several years investigations of many carefully purified liquid hydrocarbons have been carried out with short square pulses and interelectrode gap measuring several tens of microns. In these experiments quite high values of E_{br} were obtained. Some authors are inclined to consider these values to be genuine for very pure liquids. However, the smaller values of E_{br} obtained by other investigators, even though they resulted with other voltage forms and with a wider spark gap, are thought by the authors to be attributable to insufficiently thorough purification of the compounds under study.

On the basis of such affirmations, for instance, in the review (L. 87), an unconvincing attempt is made to cast doubt on the established connection between E_{br} and Σ of the liquids (L. 34) as well as the existence of partial breakdowns in the predischarge time period for xylene (L. 89).

From the experimental material which exists, actually it is possible to arrive at the conclusion that E_{br} of the same liquid grows with a reduction in the interelectrode gap with l. An especially sharp growth is observed with a decrease in l down to tens of a micron, but this depends also on the wave form of the applied voltage and on some other factors.

So far there are no universal investigations which would have captured the effect of all possible factors for one arbitrary liquid. There are only the data on the change in E_{br} for various liquids, for various voltage wave forms and in a rather narrow range of interelectrode gap widths.

In Fig. 25 curves are presented for E_{br} of some liquid hydrocarbons as a function of l. The solid curves were obtained with DC voltage (L. 90) and the dotted curves with square pulses (L. 20 & 91). From the curves it is seen that for spark gap widths measured in microns, values of E_{br} are rather large (larger than 4 Mv/cm). With an increase in l up to 20 microns a sharp drop in E_{br} occurs. In the case of a further growth in l the rate of this drop is drastically slowed down, but judging from other reports the indicated situation still does not indicate that the values of breakdown voltage asymptotically approach some limiting value.

The curves in Fig. 26 represent the same kind of dependence for $E_{br} = f(l)$, but for wider interelectrode gaps. These curves were obtained by various investigators (L. -4, 62, 76, 92-96). In all cases an increase in E_{br} was established when l was decreased. The steepness of the growth in E_{br} depends on the purity of the liquid.

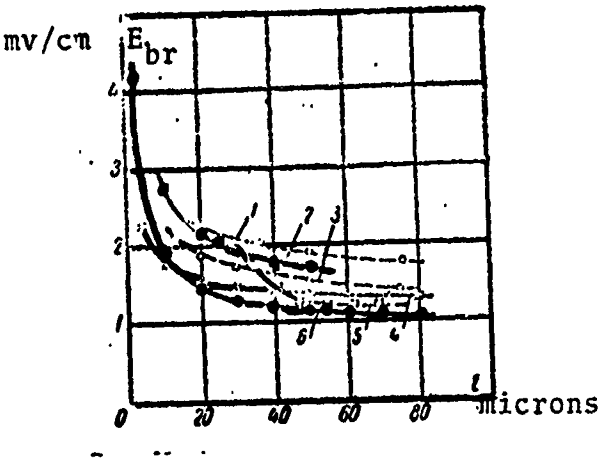


Fig. 25. The dependence of E_{br} On Spark Gap Widths For Various Hydrocarbon Liquids

1- $C_{14}H_{30}$: 2- $C_{10}H_{22}$: 3- C_6H_{14} : 4- 2-Methyl Heptane: 5- C_6H_{14} : 6- C_6H_{14}

On the basis of the experimental material obtained for the indicated dependence an empirical formula has been proposed

$$E_{br} = A + \frac{B}{I},$$

where 1 is measured in centimeters.

Numerical values for the constants A & B for certain liquids are presented in Table 13.

Table 13. Numerical Values of the Constants A & B in Formula (11) For Certain Liquids

Liquids	Electrodes	A, Mv/cm	B, Mv/cm
Turpentine	Flat	0.243	6.00
Xylene	"	0.402	12.00
Benzene	"	0.527	6.33
Petrolium	"	0.576	6.06
Transformer Oil	Spheres r = 1.23 cm	0.090 - 0.170	10.0 - 9.0
same	Spheres r = 2.5 cm	0.100 - 0.180	8.0 - 3.0

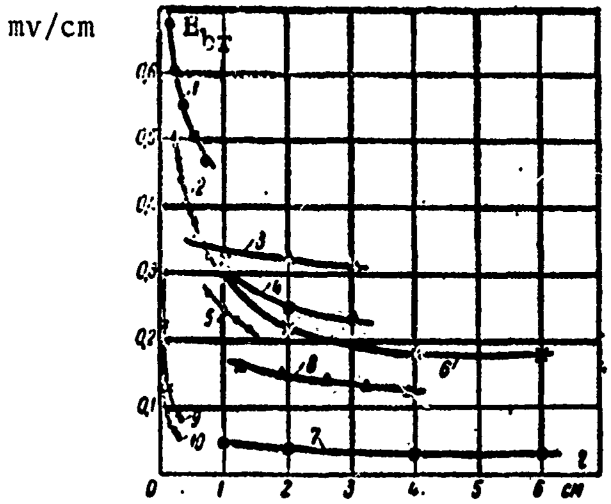


Fig. 26. The Dependence of E_{br} on the Interelectrode Distance For DC and AC Voltages (50 hz)

1- Xylene according to Sorg; 2- Ligroin and Hexane according to Sorg; 3- Transformer oil, electrodes: small sphere (-) and spherical section according to Nikuradze; 4- The same, but positive sphere; 5- Transformer oil according to Sorg; 6- Transformer oil, purified and dried, according to Dreher; 7- The same but not purified; 8- Transformer oil, according Peak; 9- Juniper oil according to the data of the Association of Electrical Researchers, (ERA); 10- The same for almond oil.

It is necessary, however, to observe that some investigators did not establish such a dependence (L. 96-98). Apparently in the given case secondary factors exerted a strong influence on the results of the measurements and the obtained must be considered atypical.

In Fig. 27 a curve is obtained for sovtol for pulse voltage pulse wave lengths of 40 microseconds and with electrodes consisting of a sphere and a plane. Sovtol, as is well known, consists of 75% pentachlorodiphenyl (sovol) and 25% trichlorobenzene (sovtol 1). This liquid dielectric has specific gravity 1.5 -1.55. Its viscosity at 65°C is no higher than 10 centistokes and $\varepsilon = 3.8$. The boiling temperature is equal to 240 -320°C. There will be something to say later about the structural features of pentachlorodiphenyl (sovol).

From this curve it is seen that with an increase in spark gap width E_{br} falls very steeply. A comparison of curves 6 & 7 in Fig. 26 shows that for poorly purified transformer oil the reduction in E_{br} is very small. However, for un-degassed N-hexane this fall in the range of 1 from 0.025 to 0.5 mm may be considered substantial (Table 14). Apparently, besides the degree of purification, an important factor is the degassing of both the liquids and of the electrodes.

From Table 14 it is also clear that the spread in values of E_{br} for un-degassed N-hexane is quite large.

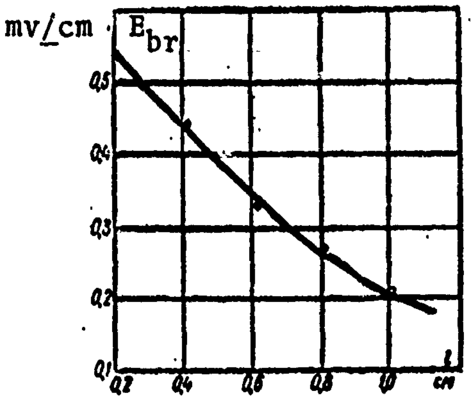


Fig. 27. The Dependence of E_{br} of sovtol on inter-electrode distance for pulse voltage (according to Panov and Mravyan)

A very noticeable drop in E_{br} for DC voltage is observed also for silico-organic liquids (silicone oils) (L. 27). They represent a metallo-organic polymer, obtained by means of hydrolysis and a subsequent condensation of dimethyldichlorosilane or its analog.

Silicone oils do not yield to the action of oxygen at temperatures up to 150°C. They preserve their coloration and do not decompose; they do not react with a majority of metals and plastics. In contrast with transformer oils, they do not cause any swelling in natural rubber; they mix well only with the higher alcohols and solvents (ether, ethyl acetate, benzene, chloroform, CCl_4, etc); with the lower alcohols, water and lubricating oils they do not mix. Only concentrated acids and alkalis interact with them.

These oils may be utilized for impregnating paper (electrical) condensors, and also for filling transformers. It is not recommended that they be employed for extinguishing electrical arcs in oil circuit contact breakers. The electrical strength of technically pure silicone oils (without special purification) for $l > 1$ mm amounts to about 300 kv/cm.

Table 14. Values of the breakdown voltage of N-hexane with DC voltage and for interelectrode distances (L. 56)

Width of Spark Gap mm	breakdown voltage, Mv/cm		
	average value	minimum value	maximum value
0,500	0,731	0,575	0,851
0,250	0,749	0,543	0,912
0,100	0,788	0,674	0,905
0,050	0,797	0,622	0,943
0,025	0,824	0,607	1,040

Note: Liquid and electrodes not degassed.

Some physical properties of (English) liquids which were investigated (type DC-200) are reported in Table 15. The data for N-pentane (L.27) are presented here also for comparison.

In Fig. 28 curves characterizing the dependence $E_{br} = f(l)$ of these liquids for DC voltage are presented. Before the experiments the liquids were taken through distillation, filtration, degassing and drying (L. 27).

It was noticed that at the time of breakdown for such liquids an opaque deposit forms and E_{br} decreases noticeably (to a significantly greater extent than for liquid hydrocarbons).

The dependence $E_{br} = f(l)$ in the most general outline may be explained in the following manner. Let us suppose that break-

Table 15

Physical properties of silico-organic liquids studied.

Properties	Type of silico-organic liquid				
	dimer	trimer	tetramer	pentamer	n-pentane
Chain length n (see Fig 78)	0	1	2	3	-
Boiling point, °C	99.5	152	192	230	36
Melting point, °C	-68	-86	-76	-84	-130
Viscosity at 20°C, centipoise	0.65	1.04	1.53	2.06	0.367
Specific gravity at 25°C, g/cm^3	0.761	0.818	0.853	0.871	0.626
Molecular weight	162	236	310	384	72

down is effected by electron avalanches which form in the course of shock ionization. The growth in current in this case, as is well known, proceeds according to an exponential law

$$J = J_0 e$$

where α is the ionization coefficient. If αl attains a certain value, then the gap between electrodes becomes highly conducting, i.e., it will break down.

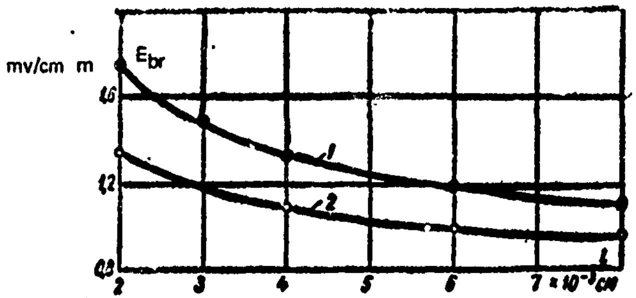


Fig. 28. Dependence of E_{br} for silico-organic liquids (silicones) on interelectrode distance - electrodes are spheres of *d* = 13mm 1- tetramer; 2- dimer

Let us denote the mean free path of free electrons by λ. With reference to the fact that the part of the electron path which is greater than x will be equal to $e^{-x/\lambda}$, it is possible to reason in a similar way that when e is about equal to E_{br} the number of regions k in which the electron energy attains a critical value W_0 will be equal to:

$$k = e^{-W_0/e\lambda E_{пр}};$$

here e in the exponent is the elementary charge (L. 20).

Let us suppose that on the length d < λ for regions k shock ionization must take place. For interelectrode distance *l* m ionizations or stages of electron multiplication are necessary in order for breakdown to be realized. Then for inelastic collisions

After taking the logarithm we obtain:

$$E_{br} = \frac{W_i}{e\lambda \ln \frac{l}{m\lambda}}.$$

Thus with only the most rudimentary assumptions, taking account of shock ionization alone, one may obtain a dependence $E_{br} = f(l)$ which is close to the dependence observed in experiments for the breakdown of several liquid dielectrics.

From the data presented it follows that in evaluating an insulating liquid in terms of its breakdown voltage it is necessary to indicate the width l of the spark gap at which this voltage was determined. But in addition to l, other factors also exert a strong influence on E_{br}.

For liquid dielectrics consisting of some specified quantity of distributed impurities, E_{br} may depend also on the electrode area. In this case an important role is undoubtedly played by statistical factors, for instance the random concentration of impurities, moisture, gas bubbles, etc.

For carefully purified liquids the electrode area has a telling effect only in the case of small interelectrode distances.

In Table 16 some numerical data are presented which were obtained in experiments with thoroughly purified transformer oil with DC voltage and with $l = 100$ microns (L. 37). The density of the oil was equal to 0.88, the viscosity 28 centistokes and the average molecular weight 310.

The formation of electron avalanches in shock ionization, as is well known, depends on the width of the spark gap and on the number of initial electrons n_0 ($n = n_0 e^{\alpha l}$).

For small l the formation of avalanches is more difficult. Therefore the breakdown voltage of oil depends on the electrode area. The larger the metallic surface of the cathode, the more burrs, projections, protuberances and all other types of irregularities will be on that surface, and from these the electron emission will go on at a much more intense level.

Table 16. The effect of electrode shape and area on the breakdown voltage of transformer oil - electrodes made of stainless steel

Electrode's Shape	electrode's diameter in mm	breakdown voltage, Mv/cm
spheres	12,7	1,225
hemispheres	25,4	1,060
discs with effective area, 3 mm	—	0,845

For large l avalanche formation is not limited and breakdown formation may begin with an insignificant number of initial electrons. In this situation the breakdown voltage has not yet come to depend on electrode area (L. 99).

Some reduction in the values of E_{br} has been dectected for N-hexane when the electrode area is increased. Breakdowns occurred for short square pulses and for small spark gaps (L. 100). There is information on this type of influence also in reference (L. 22).

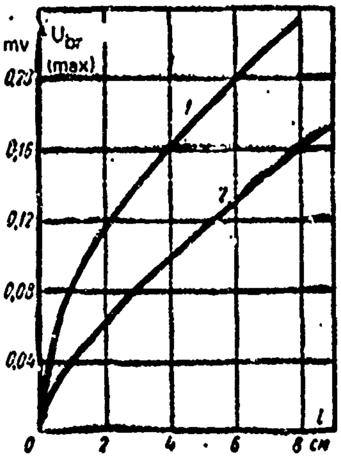
3-3. The Effect of Electric Field Non-uniformity On the Value Of U_{br}

Experiments showed that besides the spark gap width and the electrode area, U_{br} for liquids is determined to a significant degree by the geometry of the electric field.

Curves of the dependence $U_{br} = f\ (l)$ for transformer oil with electrodes consisting of a point and a plane, the point having either polarity, are presented in Fig. 29. It follows from the curve that with a negative point U_{br} is greater than with a positive point. As in the case of gas gaps, a clearly expressed polarity effect is observed in breakdowns of transformer oils (L. 101). The difference in the values of U_{br} grows with an increase in the distance between electrodes for DC voltage.

The polarity effect is explained by the differing mobility of electrons and positive ions. In the case of the positive point at the beginning of shock ionization electrons leave for the point, leaving the less mobile positive ions. In the further process of shock ionization electrons arrive into this positively charged column and form a narrow, highly-conducting projection which grows along the direction toward the cathode plane. The sharp field in homogeneity formed in this manner is maintained for the whole time of breakdown formation. In such a situation the point, so to speak, moves toward the plane. Therefore the dielectric breaks down at significantly smaller voltages.

Fig. 29. Dependence of U_{br} for transformer oil having an average degree of purity on interelectrode distance for DC voltage. 1- Negative point and plane; 2- positive point and plane.



In the case of a negative point at the beginning of shock ionization the electrons move from it into the area with the smallest field intensity. There they are captured by molecules of the liquid and form negative space charge, which to a significant degree smooths out the sharp field in homogeneity at the point. The field intensity is therefore reduced, and for a gradual development of breakdown the voltage at the electrodes must rise. A positive space charge consisting of ions reinforces the field intensity at the point and electrons will also enter the positive column - originating from both cold emission from the cathode and from shock ionization. A highly-conducting projection is also formed.

In the movement of this projection to the plane the field intensity rises and the process of shock ionization begins. The electrons head for the positively-charged plane and leave the column of uncompensated positive charge, but the loss is already at the plane. Shock ionization may also begin from the field intensity enhancement at the head of the column which is facing the point, and the highly-conducting projection will grow in the reverse direction. This third phase of development of the discharge is called the principal or the reverse discharge in contrast to the first - avalanche - discharge and the second discharge when the highly-conducting (plasma) projections are formed. The principal discharge is usually characterized by rapid advance and intense radiation.

In the case of a positive point as the streamer approaches to the plane, a column is formed from the negative charge, which also stimulates a reverse discharge.

The existence of shock ionization at points such as discussed above is proved in experiments with transformer oil and distilled water (L. 103 - 105). It was ascertained that the formation of breakdown as in gases, begins at the electrode with the greatest curvature. With significant limitation of the discharge current an intermittent development of breakdown (stepped leader process) is observed. In the case of two points this process begins at both electrodes. To the extent that the leader progresses into the depth of the gap its rate suffers a decrease. These experiments were carried out with a rapidly rotating chamber and with a cathode ray oscilloscope (L. 103).

When the distance between the needle and the plane l = 170cm and with a pulse voltage of 80 kv, multiple risings and fallings of the electrical conductivity σ for distilled water (L. 105) were registered on the high-voltage cathode ray oscilloscope during the time over which the pulses were acting. These excursions are explained by shock ionization and by the capture of electrons by highly polar molecules of the liquid.

From the curves of Fig. 30 some idea may be gotten of the effect of polarity of the point when the interelectrode distances are comparitively large. Experiments were performed (L. 102) with transformer oil of an average degree of purity with pulsed (curves 1 & 2) and with AC (50 hz) voltages (curve 3). Comparing curve 3 of Fig. 30 with curve 2 of Fig. 29, it is seen that the values of U_{br} for the same interelectrode distances in the case of AC voltage are almost the same as with the positive point (DC voltage). The time factor does not play any particular role here inasmuch as at 50 hz a half period is fully sufficient for breakdown formation. However, the influence of time begins to take effect when pulses are used. The breakdown voltage rises (see curves 1 & 2 in Fig. 30).

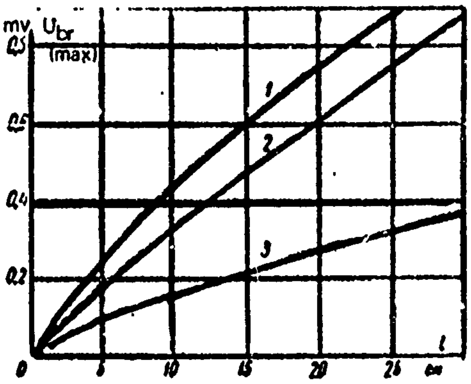
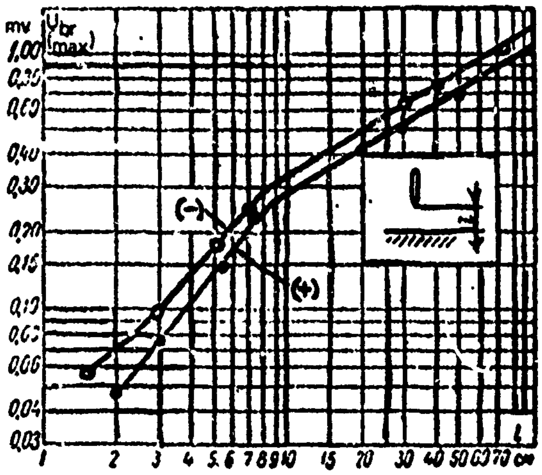


Fig. 30. Values of U_{br} for transformer oil occurring between a point and a plane for various interelectrode distances. 1- negative point; 2- positive point; 3- AC voltage.

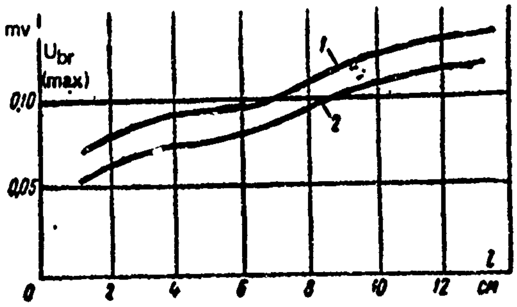
The same kind of curves, obtained in breakdown with wider spark gaps, are presented in Fig. 31 for technically pure transformer oil. The breakdowns occurred at a temperature of 15 to 20° C and with pulse voltage with wave lengths (the time taken by the largest amplitude in its drop to half value) of 40 microseconds (L. 95). The slope angle of the curves $U_{br} = f(l)$ for $l > 8$cm decreases, i.e., the values of U_{br} in a unit of length within the spark gap becomes smaller. Apparently under this condition formation of breakdown is improved. In Fig. 30 such a break in the curves is not noticeable. For the same values of l the U_{br} values according to the curves of Fig. 30 are greater than according to Fig. 31. This difference as well as the absence of a break in the curve must evidently be attributed to the deeper pulses with which the curves of Fig. 30 were recorded.

Fig. 31. Breakdown voltage U_{br} for pulses as a function of the distance l between the point and the plane. The signs (+) and (-) refer to the point.



In Fig. 32 data on U_{br} for sovtol are presented (L. 95). Breakdowns of the gaps between a point and a plane were produced also with pulses of wave lengths 40 microseconds and at temperature 20° C. It was determined that for interelectrode distances of l = from two to three cm the value of U_{br} for sovtol and for transformer oil differ very little. But for larger values of l curves diverge sharply. In this case the value of U_{br} for sovtol is smaller than for transformer oil. Such a divergence is undoubtedly stipulated by the physical-chemical features of the liquids being compared. It was noted that under the influence of strong electrical fields the sovtol decomposes with profuse evolution of carbon black.

Fig. 32. Breakdown voltages for sovtol for various distances between the point and the plane. 1- negative point; 2- positive point.



In the investigation of incompleted breakdowns of transformer oil between a point and a plane (1 = 25mm) it was ascertained that the discharge channel serves as a source of intense short-wave radiation. The appearance of this radiation was recognized by the diffuse blackening of silver bromide photographic paper which was placed perpendicular to the point at various distances from it. The experiments were conducted with aperiodic pulses with a rise time of 1 microsecond and a wave length of 50 microseconds (L. 106).

In the case of a positive point the radiation occurs only for a voltage greater than 90 kv. It becomes quite considerable at a voltage of 190 kv. In the case of incomplete breakdown, blackening of photographic paper placed at the plane at a distance of 25 mm is already occurring when the length of the channel from the point is only 7 mm.

Somewhat different conditions are created with a negative point. The radiation in this case becomes highly noticeable even at comparitively small voltages (105 kv). This leads to excitation and step-wise ionization of the molecules of oil. The process of breakdown development accelerates.

Studying the Lichtenberg figures obtained in breakdowns and spark overs of the same transformer oil, the author (L. 106) separated a special stage in the channel condition, characterized by a high degree of ionization. This condition is called the thermo-ionization state. In the work mentioned it is asserted that radiation arises under just such a condition of the channel.

In reference (L. 107) an account is given of an investigation of the electrical strength of transformer oil under the action of pulses with damping oscillations. The oscillation frequency varied from 20 to 500 khz. It was established that the breakdown 50% voltage $U_{br_{50}}$ for the negative point and plane, as in the case of pulses without oscillation, was 10 to 30% larger than for the positive point.

For pulses with damping oscillations and with distances between the positive point and the plane of l = 25 & 30 mm the value of U_{br50} has a maximum. It was fixed at frequencies 70 & 120 hz respectively (see Fig. 33). The values of U_{br} for a pulse wave with a rise time of one microsecond and a wave length of 50 microseconds but without damping oscillations, turned out to be significantly smaller; in the figure these are denoted by a, b, and c.

If we supply pulses with amplitude U N times to the material under investigation, then the breakdowns may occur not indefinitely but only n times. Then the probability of occurrence of breakdowns will be equal to $p = \frac{n}{N}$. In increasing or decreasing the largest amplitude of the voltage pulses, the breakdowns will occur more or less, and the probability of their occurrence will be determined by the size of U. The results obtained may be presented in the form of a curve, by plotting, for instance, p = f (U) from 0 to 100% along the axis of the ordinate and U along the axis of the abscissa. Then the value of U_{br50} will correspond to p = 50%. In doing this one should watch that the electrodes of the measuring vessel and the liquid under study are not seriously damaged by the electrical spark.

3-4 The Dependence of E_{br} and U_{br} On the Duration of Voltage Application

It is quite obvious that for the development of the breakdown process, as for any process as a matter of fact, a fully specified amount of time is necessary. Under real conditions the formation of electron avalanches proceeds in a medium whose molecules counteract this process by capturing free electrons and taking them out of the system. The formation of breakdown is therefore drawn out over some amount of time. If the duration of voltage application is less than this time, a breakdown will not occur at the given E. It will be necessary to increase the voltage at the electrodes, so that $\alpha = f$ (E). A large number of experiments con-confirms this observation.

Ordinarily, even highly purified liquids contain some amount of impurities and gases, and even moisture. Any or all of these ingredients exert no noticeable effect on E_{br} for very short exposures, as will be shown below, but for prolonged application of voltage they cause a reduction in this quantity.

Some data on the drop in E_{br} as the holding time is increased within the limits from 20 to 7000 seconds are presented in Table 17 for comparatively large interelectrode distances (L. 108).

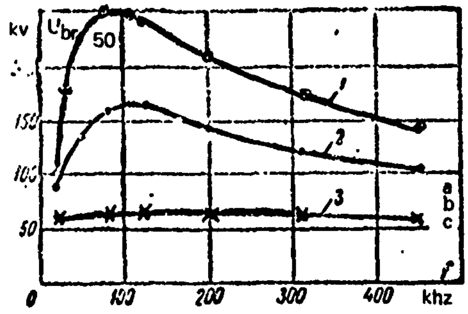


Fig. 33. Dependence of the breakdown 50% voltage on a frequency of damping oscillations for a pulse wave with a positive point and plane at a distance 1. 1- 1 = 35 mm; 2- 1 = 25 mm; 3- 1 = 10 mm; a,b, and c are values of U_{br} for the indicated 1 with pulses without oscillations with a life time of one microsecond and wave length 50 microseconds.

It is seen from Table 17 that the reduction in E_{br} is noticeable even for holding times counted in tens of minutes. At a somewhat higher temperature, in order to obtain the same values of E_{br} as were obtained at 14° C, the holding time had to be increased.

If the value of the initial electrical conductivity σ played a significant role in the formation of breakdown, then the relationship would be reversed, inasmuch as σ at 40° C is, of course, greater than at 14° C. The mobility of ions at 40° C in transformer oil is also greater than at 14° C. Apparently, in the development of breakdown, a decisive role is played by such other factors.

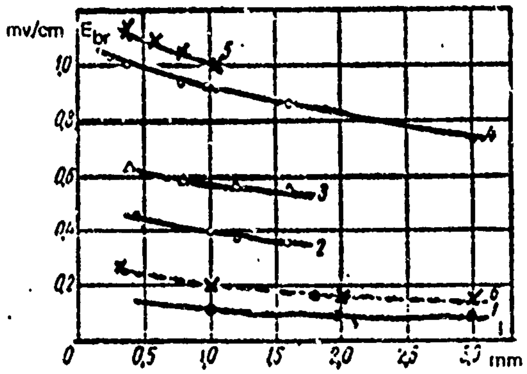
In Fig. 34 curves for the dependence E_{br} = f (1) for transformer oil are presented for various holding times within the range 1.3 x 10^{-8} to 10^{2} sec. From these curves it is clear that as the voltage application time is shortened the values of E_{br} rise rapidly. For instance, with a time of 1.3 x 10^{-8} sec and 1 about 0.5 mm, E_{br} > 1 mv/cm (L. 84).

Table 17. Dependence of breakdown voltage for pure transformer oil on the application time of a DC voltage..

Holding Time, seconds	Breakdown Voltage at 14° C, Mv/cm	Holding Time, seconds	Breakdown Voltage at 40° C, Mv/cm
30	0,160	20	0,150
50	0,135	350	0,130
100	0,120	2800	0,120
250	0,105	7000	0,110
350	0,090	—	—
1400	0,080	—	—

Note: The electric field is close to the equilibrium field.

Fig, 34, The dependence of E_{br} of transformer oil on on the interelectrode distance for varying duration of voltage application τ. 1- DC voltage τ = 100 sec; 2- the same, but τ = 3.3×10^{-4} sec; 3- the same, but τ = 4×10^{-6} sec; 4- the same, but τ = 1.2×10^{-7} sec; 5- the same, but τ = 1.3×10^{-8} sec; 6- AC voltage 50 hz.



The change in U_{br} for transformer oil with various holding times, but with a spark gap width of 1 = 20 mm between a sphere of d = 50 mm and a plane is presented by the curve in Fig. 35 (L. 95). In this figure dotted lines indicate the region that was not examined. For the indicated gap width 1 a rather sharp increase in U_{br} is observed for holding times τ smaller than 10^{-5} sec. For $\tau > 0.1$ sec, E_{br} changes little.

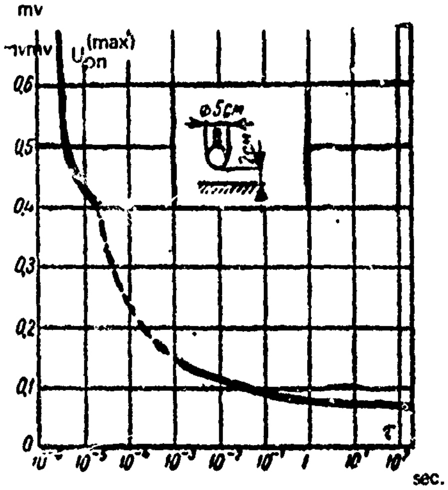


Fig. 35. Volt-time dependence for technically pure transformer oil.

For radically inhomogeneous fields a more complicated dependence has been established, as suggested by the data of Table 18 (L. 109). The signs of the potential (+) or (-) in this table refer to the point.

It is worthwhile to give some attention to the comparatively small values of U_{br} for a pulse duration of $\tau = 1.4 \times 10^{-3}$ sec; the values obtained were even smaller than for DC voltage. For shorter holding times U_{br} increases sharply.

It might be supposed that before the beginning of breakdown formation, in the comparatively slow rise in DC voltage, a zone of space charge forms near the point and the field inhomogeneity, as already mentioned, flattens out partially. But over the time of 1.4×10^{-3} this zone is apparently not able to form and the breakdown is at a smaller U_{br}. In the case of an exposure of 1.4×10^{-5} sec and smaller the space charge zone is all the more incapable of forming, but for a gradual development of breakdown with the given voltage the time was insufficient. For this development to occur the voltage had to be increased. Secondary processes were not able to manifest themselves with such holding times.

Table 18. The dependence of breakdown voltage for transformer oil on duration of voltage application for various spark gaps.

Spark Gap Width, cm	Breakdown Voltage, kv							
	OC. Voltage		tau = $1.4 \cdot 10^{-3}$ sec		tau = $1.4 \cdot 10^{-5}$ sec		tau = $1.4 \cdot 10^{-6}$ sec	
	−	+	−	+	−	+	−	+
1	62	50,5	46	32	73	44	150	100
2	97	73,0	67	49	132	82	—	—

The dependence $U_{br} = f(\tau)$ of technically pure transformer oil for a wider spark gap between the point and the plane is presented in Fig. 36 (L. 95). The experiments were conducted with pulses having voltage rise time ranging from 0 to a maximum value (wave front) of 1.5 microseconds and having a wave length of 40 microseconds. It was possible to obtain short holding times by including, in the parallel to the sample under study, an air gap between spheres, which broke down upon reaching a specified voltage corresponding to the given holding time. The voltage was thereby reduced from that of the object under study.

Unfortunately, it is impossible from the curves of Fig. 36 to establish the existence of a minimum in U_{br} (see Table 18) for holding times of around 1^{-3} sec, since this region of exposures remained outside the region investigated (dotted lines). It is possible that for such a large distance between the needle and the plane, namely 20 cm, such a minimum would not exist at all. For a positive point the value of U_{br} in the range of holding times from 0.1 to 100 sec is practically unchanging. In this figure along the axis of the ordinate on the right are plotted the values of the pulse coefficient beta, which shows how much greater U_{br} is for shorter effects with voltage than with prolonged ones.

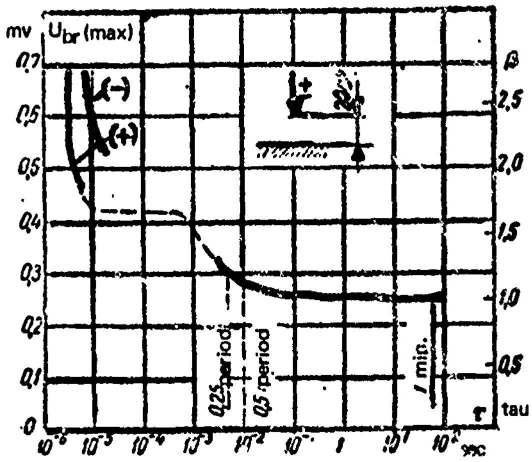


Fig. 36. Breakdown voltages for technically pure transformer oil with various durations of voltage application.

For each region of holding times within the range from fractions of a microsecond to one minute the change in U_{br} for transformer oil is shown by the curve in Fig. 37 for 1 = 12.7 mm, referring however to the distance between discs of various diameters (L. 95). The steepness of the growth in values of U_{br} for various τ turned out to be also not uniform. For instance, in the interval of τ from 10 to 0.5 microseconds as also according to the curve of Fig. 35, U_{br} rises sharply but barely changes with longer holding times - up to 10^3 microseconds.

In principle the same type of trend in the change of E_{br} (L. 110) would be revealed for pure, but not degassed, xylene and hexane (Fig 38). The curves are registered for aperiodic pulses. Gaps of 0.5 mm experienced breakdown. According to these curves, however, it is impossible to say anything about the change in E_{br} for holding times in the range from 10^{-6} to 10^{-3} sec and from 1 to 10^{2} sec it is very noticeable.

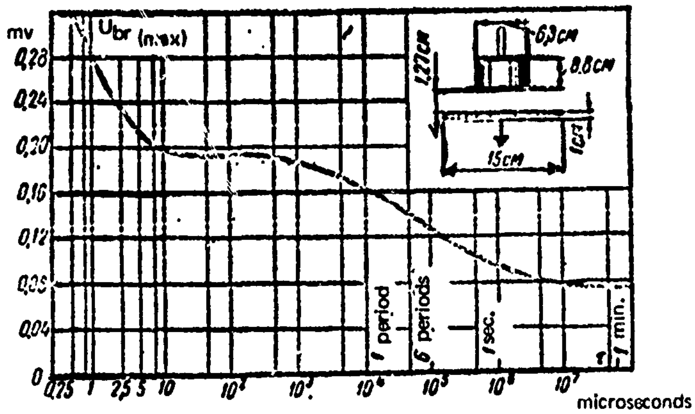


Fig. 37. The average volt-time characteristic for technically pure transformer oil.

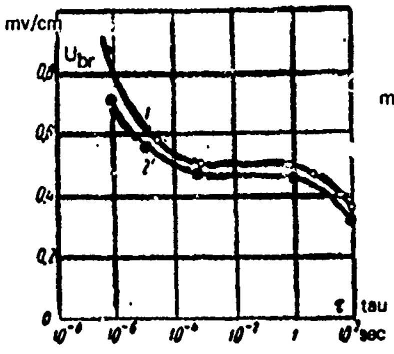
Experiments which were set up more carefully with respect to the change in E_{br} for small holding times showed that in the range from approximately 2 to 17-23 microseconds E_{br} was practicably unchanging (L. 111). Such experiments were performed with carefully purified ethyl alcohol (Fig. 39) and benzene with square pulses and with distances between the polished spheres of several tens of microns. For holding times less than 2 microseconds E_{br} for ethyl alcohol increases by a factor of almost two in comparison with E_{br} for $\tau >$ two microseconds, and for benzene this increase is even greater.

Unfortunately there are no data on the change in E_{br} for these liquids with longer pulses, but on analogy with the curves of the preceding drawings one may hypothesize the existence of a second drop.

A quite interesting situation is the observation that even such a very poor dielectric as distilled water, for short exposures and spark gap widths of several tens of microns, has an E_{br}

greater than 1.5 mv/cm (see curve 1 of Fig. 40). On this same drawing a curve for pure ligroin is also presented for comparison (L. 35.). It is recorded for the same experimental conditions.

In contrast with ligroin, benzene and ethyl alcohol, the value of E_{br} for distilled water drops without interruption when τ is increased. Th. undoubtedly tells us something about the large electrical conductivity of the indicated liquid. However, the most abrupt increase in E_{br}, as for other comparable liquids, occurs for holding times shorter than 2 microseconds.



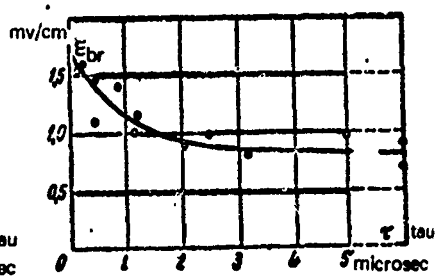


Fig. 38. The dependence of E_{br} on pulse duration for pure but un-degassed liquids.
1- xylene; 2- hexane

Fig. 39. The dependence of E_{br} of ethyl ether alcohol on duration of an applied square pulse voltage.

On the basis of the experimental data presented above it is possible to form the conclusion that for interelectrode distances of several tens of microns and for exposures less than 2 microseonds the liquids lose to a considerable extent their individuality with respect to E_{br}. This means that their chemical composition. structure, polarity, electrical conductivity, and consequently their impurities in moisture content do not exert any substantial influence on E_{br}.

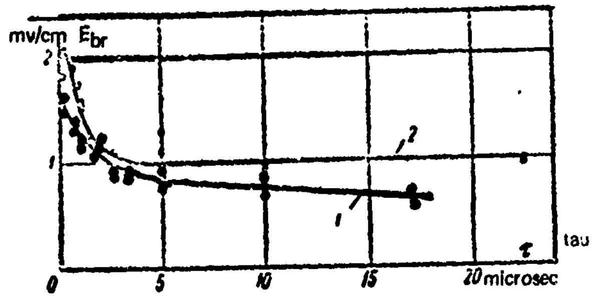


Fig. 40. The dependence of E_{br} of distilled water and ligroin on duration of pulse imposition for a uniform field (square · pulses). 1- water; 2- ligroin.

The experiments showed further that for small spark gaps there is a definite relationship between the gap width and the shortest duration of voltage application for which a growth in E_{br} is initiated. This relation is expressed in the curves of Fig. 41 (L. 91) for N-hexane (normal, not isomeric). The experiments were performed also with square pulses and with spherical electrodes made of phosphor-bronze. These electrodes were polished with diamond dust. The liquid under study was distilled and subjected to electrical purification.

From the curves of Fig. 41 it follows that the minimum time τ_0, below which a growth in E_{br} begins, depends on the distance between electrodes 1. The greater 1, the greater τ_0. However, the minimum value of the breakdown voltage E_{br} for distances greater than 47 microns turned out to be the same. For smaller 1 it increases.

For pulses for a duration less than the threshold value τ_0 each curve in Fig. 41 may be represented by the empirical formula

$$E_{br} = \frac{C_1}{(\tau - \tau_n)^c},$$

where lower c and C_1 are constants, and τ is greater than τ_n.

The values of the quantities entering into formula (14) for N-hexane are presented in Table 19.

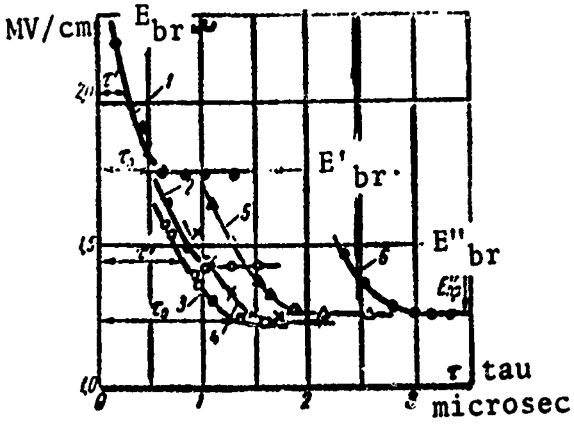


Fig. 41. The change in E_{br} of N-hexane for various square pulse durations and interelectrodes distances 1. 1- 1 = 33 microns; 2- 1 = 41 microns; 3- 1 = 47 microns; 4- 1 = 54 microns; 5- 1 = 61 microns; 6- 1 = 68.5 microns.

The authors of reference (L. 91) are of the opinion that the time τ_0 is the time necessary for obtaining with electrons from the applied field that energy which is sufficient for ionization of the molecules of the liquid. It is also necessary for the formation of a highly conductive bridge between the electrodes. In this way τ_0 must be connected with the movement of electrons and ions and consequently must also depend on their mobility and on the distance between electrodes 1.

Table 19. Values of the quantities in formula (14) for N-hexane.

Spark gap Width 1, (microns)...33	41	47	54	61	68.5
τ_0 (microseconds)..............0.6	1.1	1.2	1.6	1.9	2.8
r (microseconds)..............0	0.1	0.1	0.1	0.5	1.5
C_1^n (MV/cm).....................2.7	2.6	2.5	2.6	2.6	2.0
c............................0.3	0.3	0.3	0.4	0.4	0.2
E_{br} (MV/cm)....................1.76	1.43	1.24	1.24	1.26	1.26

In Table 20 data are reported for the values of τ_0 in N-hexane and for a time τ_p required for transit of the spark gap 1 by positive ions. This time is computed from the relationship

$$\tau_p = \frac{l}{k_p E_{up}}.$$

The mobility k_p is determined from experiment. It turns out equal to $8.9 \times 10^{-4} cm^2/sec$ v.

The quantity τ_0/τ_p, as follows from Table 20, has almost no dependence on the spark gap width 1. Determination of this ratio also for other liquids with different viscosities.

Table 20. Numerical data for τ_0, τ_p and τ_0/τ_p for N-hexane.

Spark Gap Width l (microns)	33	41	47	54	61	68,5
τ_0 (microseconds)	0,6	1,1	1,2	1,6	1,9	2,8
τ_p (microseconds)	2,26	3,46	4,6	5,25	5,85	6,55
τ_0/τ_p	0,3	0,3	0,3	0,3	0,3	0,4

The mobility k_p was computed from the formula (L.74):

$$k_p = c\eta^{-3/2},$$

where η is the viscosity;
c is a constant.

The relations found between τ_0 and τ_p are represented by the curves in Fig. 42. For polar and non-polar liquids straight lines were obtained, but with different angles of slope to the axis of the abscissa.

The time τ_0, which, as it was observed, may be equated with the time for breakdown formation, is equal to 1-2 microseconds for N-hexane according to the curve of Fig. 42 and is about 12 microseconds for tetradecane. Therefore τ_0 for liquid hydrocarbons must be depend also on the molecular weight. Moreover, it must be proportional to that length of time which is required by the positive ions in order to traverse the whole spark gap. This signifies that in the breakdown mechanism for liquid dielectrics even for short voltage application times a significant role would seemingly have to be played by the mobility of the ions. Such a conclusion, however, does not fit very well into the framework of existing concepts of the formation of breakdown. It is usually considered that the positive ions which possess a comparatively large decay time, as, on the other hand, the negative ions do also, are not able to exert a substantial influence on the development of breakdown for short holding times.

The conclusion in favor of a significant role played by positive ions in the formation of breakdown was not consistent with data obtained in reference (L. 35). This state of affairs was the compelling reason for carrying out supplimentary experiments.

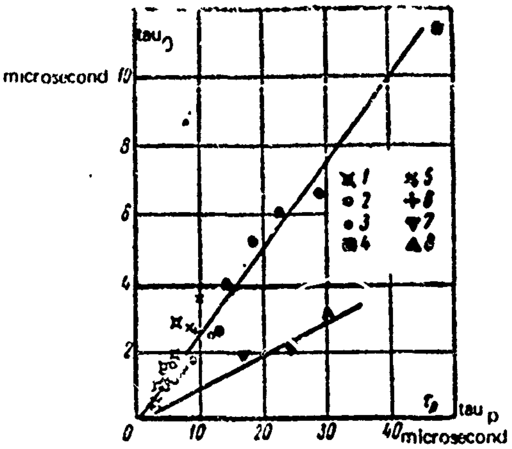


Fig. 42. Relation between τ_Q and the time for transit of the interelectrode gap τ_p by positive ions for the liquids: 1- N-hexane; 2- N-pentane; 3- N-decane; 4-N-tetradecane; 5- carbon tetrachloride; 6- ligroin; 7-methyl alcohol; ethyl alcohol.

A study was made of N-hexane and N-nonane (L. 21). These liquids differ considerably both in molecular weight and in viscosity η . For N-hexane M = 86.172 and η = 4.75 x 10^{-3} cm, while for N-nonane M = 128.25 and = 9.88 x 10^{-3} cm. Breakdowns were produced also for square pulses and in addition for very small spark gap widths ($l = 5.1 \times 10^{-3}$cm). The curves which were obtained are reported in Fig. 43. Disregarding the varying values of E_{br}, the time for breakdown formation in both cases turned out to be the same. The soundness of the conclusion reached in reference (L. 91) regarding the role of positive ions in breakdown formation were thus opened up to serious doubt.

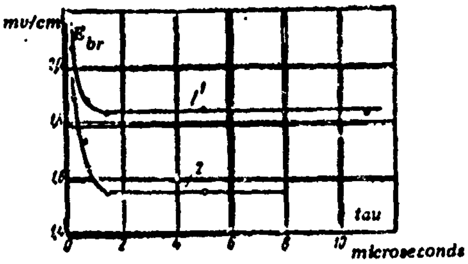


Fig. 43. The dependence of E_{br} on voltage application time using square pulses. 1- N-nonane; 2- N-hexane.

Following these reports the same experiments were again carried out for N-hexane (L. 112). Oscillograms of square pulses used for performing these experiments are shown in Fig. 44. Steel spheres were used for electrodes. The liquid was thoroughly purified with sulfuric acid, distilled and filtered prior to the experiment. The amplitude of the pulses gradually increased up to breakdown.

In the experiments the distance between electrodes was varied. Although the range of variations was quite small, still it was possible to fix the breakdown formation time corresponding to an increase l in that distance, as can be seen from the expermental curves of Fig. 45. From these data it follows that the motion of charges in the interelectrode gap would play some kind of a role or another. But it remained unclear as to whether one was justified in ascribing this to the motion of positive ions.

It is possible to conclude from the curves of Fig. 45 that for interelectrode distances of several tens of microns the time τ_0 is equal to only fractions of a microsecond. Therefore it is necessary to take strict account of the "linearity" of the pulses. When there is some departure from such linearity determination of the time of formation may be inexact.

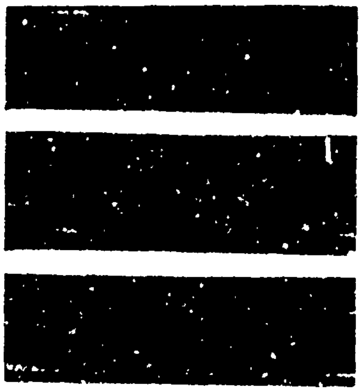


Fig. 44. Oscillograms of square pulses. The period of the graduated oscillations (pulses) on the axis of the abscisa is equal to 0.1 microsecond.

Fig. 45. Dependence of E_{br} of N-hexane on the duration of square pulses for various interelectrode widths. l. l-1=$5.08\cdot10^{-3}$cm; 2-l=$6.35\cdot10^{-3}$cm; 3-l=$7.62\cdot10^{-3}$cm; $8.89\cdot10^{-3}$cm.

In Fig. 46 the parameters are designated for one square pulse from the oscillogram in Fig. 44. Breakdown formation may begin at E_s and may come to an end on a portion of the amplitude drop following the attainment of a maximum. The time of formation would then be greater than $_m$ (Fig. 46). For a mobility of charged particles k and with

one may write for the spark gap width:

$$l = kE_m\tau_m + k\int_{E_s}^{E_m}\left(\frac{1}{r_1}-\frac{1}{r_2}\right)EdE,$$

where r_1 and r_2 are the rate of growth and amplitude drop of the pulse dE/dt. This integral must also take into account those distances which are covered by the charged particles during the growth and fall in E.

From (15) and (17) τ'_p will be equal to:

$$\tau'_p = \tau_m + \frac{1}{E_m}\int_{E_s}^{E_m}\left(\frac{1}{r_1}-\frac{1}{r_2}\right)EdE. \quad (18)$$

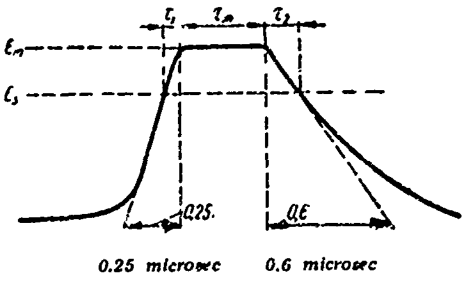


Fig. 46. Square pulse parameters

According to the oscillograms the value of E_m seldom exceeded E_s by more than 30% even for short pulses. Consequently, it is necessary to bring into the calculation only a small part of the interval of growth and fall in E (Fig. 46). Therefore it is possible to consider $dE/d\tau$ over the time τ_1 and ${}_2$ as constants. Then $r_1 = \frac{E_m}{0.25}$ and $r_2 = \frac{E_m}{0.6}$ v/cm microseconds, and the time τ'_p:

$$\tau'_p \approx \tau_m + 0{,}425\left[1-\left(\frac{E_s}{E_m}\right)^2\right]. \tag{19}$$

From these data the dependence of τ'_p on the ratio $1/E_m$ is constructed for N-hexane in Fig. 47 (curve 1). The same dependence is depicted by curve 2 for the same N-hexane ($\tau'_p = \tau_p$) according to the data of reference (L. 91). The curves obtained do not coincide. It follows form this that the positive ions in the development of breakdown do not play that role which was ascribed to them in reference (L.91), apparently because of an error in the execution of the experiment.

It is interesting to note that the breakdown formation time for liquid dielectrics with various lengths of unbranched molecule chains turned out to be about the same (see Fig. 48). The distance between steel spheres in the experiments was equal to 6.35×10^{-3}cm (L. 112).

The same situation was established also for liquids with branched chains as is clearly seen from the curves for N-hexane and for 2,4-dimethylpentane in Fig. 49. These data also give testimony to the fact that positive ions have practically no role in determining the duration of breakdown formation and that the motion of charged particles according to Fig. 45 need not be ascribed to ions.

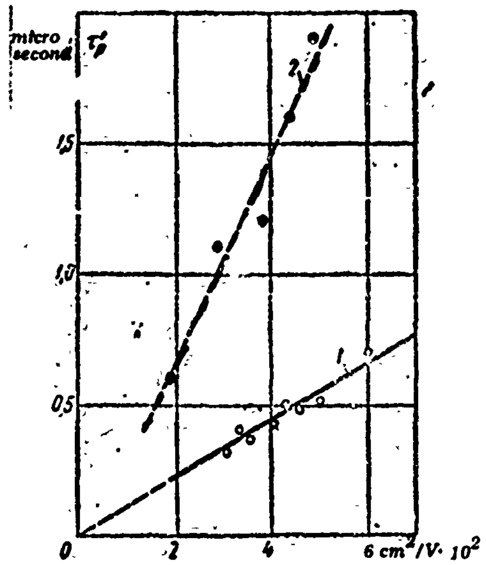


Fig. 47. The dependence of the true delay time τ in the formation of breakdown on the ratio b/ε_m for n-hexane: 1- according to reference (L. 103); - according to reference (L. 109).

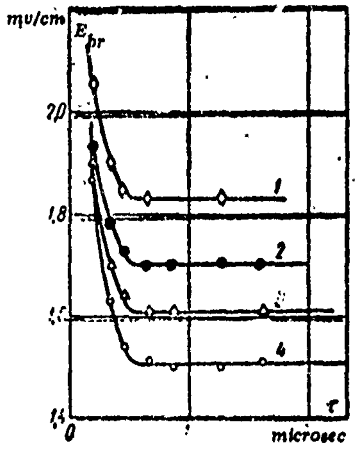


Fig. 48. The dependence of E_{br} of liquid hydrocarbons on the duration of square pulse action. 1 · n-decane; 2- n-octane; 3- n-heptane; 4- n-hexane.

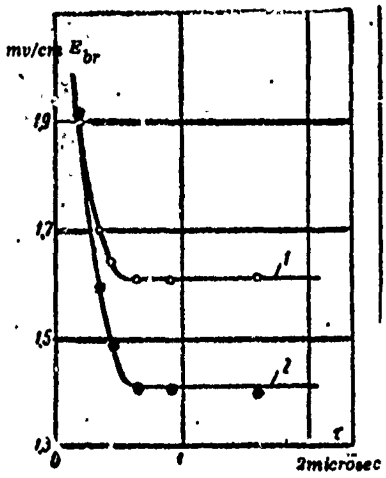


Fig. 49. Dependence of E_{br} of two isomers of heptane on the duration of square pulses. 1- n-heptane; 2- 2,4-dimethylpentane.

CHAPTER 4

The Effect of Temperature, Frequency of Applied Voltage, Electrode Material and Electron Emission from the Cathode on the Electrical Strength of Liquids

4-1. Dependence of E_{br} on Temperature

It should be mentioned that there are very few thermally stable insulating liquids and that the limits of their working temperatures are not large. The most reliable in this respect may be considered to be the silico-organic liquids (silicone oils) with working temperature up to 200° C. Further mention might be made of the insulating liquid put out in America under the name "vitamin Q" - a low molecular polyisobutylene with working temperature up to 120° C.

A liquid dielectric under the name of oktol, the domestic "vitamin Q", is synthesized also in our country. It is obtained in the co-polymerization of isobutylene and k-butylenes from the butane-butylene fraction of cracking gas (L. 49). Oktol is used in the impregnation of cables and condensers. It has the following physical and electrical characteristics:

Specific gravity	0.86 g/cm^3
Melting temperature	-10° C
Ignition temperature	165 - 175°C
Viscosity at 20°C	13,820 centistokes
Viscosity at 100°C	97 centistokes
Breakdown voltage at 20°C	0.16 - 0.18 mv/cm
Dielectric constant at 20°C	2.3
Bulk resistivity at 20° and 90°C	$3 \cdot 10^{14}$ and $5 \cdot 10^{13}$ Ohm cm
Dielectric loss angle tangent at 50hz and 20°C	10^{-3}

sented in article 5-3.

In France liquid polyisobutylenes are put out under the name "polyelectrene".

Overseas the liquid dielectric $C_{20}H_{14}F_{24}O_4$ under the arbitary trade name PFE-774 is still used for electrical condensers. This insulating liquid with $\varepsilon = 6.1$ (at 25° C and frequency 60 hz) has no color or odor, has a high thermal stability and inertness with respect to metals. At a temperature of 100° C its viscosity does not exceed 3.7 centistokes. Its ignition temperature is equal to 171° C, and it ignites at 240° C.

The overwhelming majority of other liquid dielectrics may function for a long time at significantly lower temperatures. For example, transformer oil oxidizes relatively rapidly even at 90° C. But the breakdown voltage of an unoxidized oil at such a temperature in comparison with lower temperatures either does not decrease or even increases somewhat. Upon prolonged heating an aging occurs with liquid dielectrics (see article 5-3). To predict the intensity of this process from the breakdown voltage of the fresh portion of dielectric is not possible.

In Fig. 50 experimental curves of the dependence of $E_{br} = f(t)$ are presented for transformer oil according to the data of various investigators (L. 44, 92 & 93). The degree of purification of the oils differed. In three cases the appearance of a temperature maximum in E_{br} was noted. It was not observed only in the investigation of highly purified oil (curve 1). The poorer the purification of the oil, the flatter the maximum (curve 4). Curve 5 represents the change in viscosity ε. For a steep drop in this quantity the breakdown voltage of highly purified oils changes little. In the temperature range of 7- - 100° C however the viscosity is almost unchanging, and E_{br} falls noticeably. Thus in the range from 20 to 100° C the viscosity has no appreciable effect on E_{br}.

The absence of a temperature maximun in E_{br} for thoroughly purified transformer oil is corroborated also by other investigatos (see Fig. 51) (L.65 & 113). Breakdowns were produced with DC voltage for various pressures over the oils. Reduction in E_{br} was noted for t greater than 100° C.

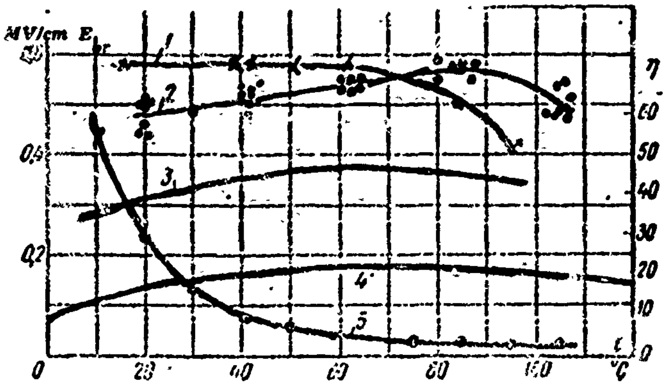


Fig. 50. Dependence of E_{br} for transformer oil on temperature and viscosity. 1- according to Nikuradze (DC voltage); 2- according to Toriyama (AC voltage); 3- according to Spats (DC voltage); 4- according to Frieze (AC voltage); 5- according to Nikuradze for viscosity.

For temperatures below zero E_{br} for oil increases (see Fig. 52). The same takes place for condenser sections made of paper with thickness 8 microns, impregnated with the same oil under vacuum. For temperatures below -40° C the oil becomes semi-solid; its density increases considerably, and along with this E_{br} also rises.

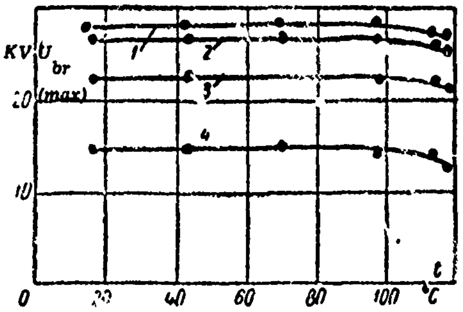


Fig. 51. Dependence of U_{br} of carefully purified transformer oil on temperature for various pressures over the liquid. 1- p = 750 mm hg; 2- p = 500 mm hg; 3- p = 250 mm hg; 4- p = 10 mm hg.

The existence of a temperature maximum for transformer oil in reference (L. 34) is explained by the general dependence of E_{br} on dielectric constant (see article 1-5). The authors of the indicated work direct attention to the fact that although transformer is not a dipole liquid it nevertheless always contains some amount of moisture and weakly polar impurities. Therefore when the temperature rise ε decreases somewhat and E_{br} increases. At 80° C the light fractions begin to boil and gas bubbles are formed in the oil, thus reducing E_{br}.

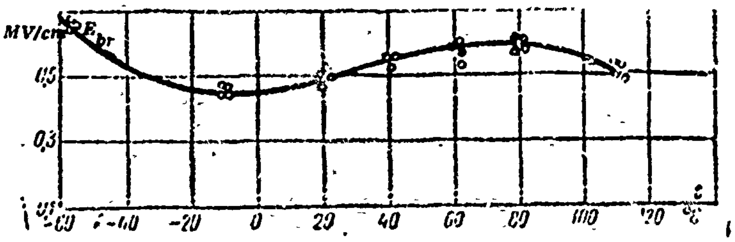


Fig. 52. Dependence of E_{br} for transformer oil on temperature with AC voltage.

One may obtain some idea of the effect of acidity on the temperature trend of E_{br} of dry transformer oil with DC voltage by reference to the curves in Fig. 53. When a small portion of naphthenic acid (about 0.05%) is added to this oil the value of E_{br} upon increase in temperature decreases noticeably (L. 45). Such additions may act in the direction of increasing the number of charged particles. In the process of prolonged use at elevated temperatures the acidity of the oil increases; therefore their breakdown voltage must also become less.

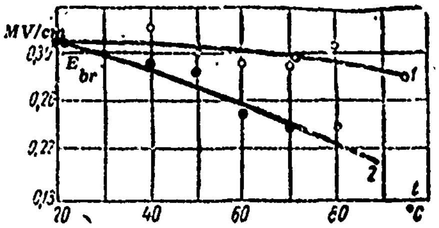


Fig. 53. Dependence of E_{br} of transformer oil on temperature. 1- dry oil; 2- the same, but with an addition of about 0.05% naphthenic acid

Over the last decade a large quantity of experimental data on the breakdown of liquid dielectrics has been accumulated for post voltages of a rectangular or almost rectangular wave form.

Formerly, the technique of generating such pulses did not provide the possibility of obtaining voltages greater than 15 to 20 kv, and therefore breakdowns were produced exclusively in gaps of several tens of microns. Because of this and especially careful measurement of distances betweens the electrodes was required as well as the exclusion of influence from any suspended particles in the liquids.

This state of the experimental technology was apparently the reason for a large divergence in the results in the various workers (L. 21 & 91). In regard to determining the temperature trend of E_{br} for n-heptane (C_7H_{16}). This liquid in both cases was thoroughly purified and therefore there are no bases for believing that the similar divergences in these cases were caused by impurities or contamination.

In agreement with the data of reference (L. 21), when the temperature rises the decrease in E_{br} and in the density of n-heptane may be represented by a single straight line; in Fig. 54 it is shown as a dotted line (curve1). The experimental values of E_{br} are indicated by circles near this line. In this experiment breakdown occurred in a 0.0084 cm gap between a mercury cathode and an anode of steel. The duration of the rectangular pulses was equal to 1.8 microsecond. The rest of the curves in Fig. 54 were obtained by other investigators also with short rectangular pulses (L. 91). The width of the spark gap in this case was equal to several tens of microns, but the electrodes consisted of steel spheres highly polished with diamond dust. Curve 4 was obtained also for n-heptane. By comparing curves 1 and 4 it is seen that the breakdown voltages from the data of reference (L. 91) is greater than those from reference (L. 21), and with an increase in temperature it falls significantly faster. A more abrupt drop in E_{br} in comparison with a decrease in density was confirmed even for other liquids (curves 2,3, and 5). It is curious to note that according to one report (L. 21) n-heptane received more careful purification.

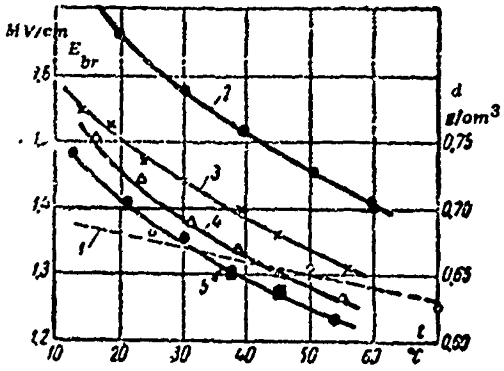


Fig. 54. Dependence of E_{br} of liquid hydrocarbons on temperature. Curve 1 is from reference (L. 104), and curves 2 - 5 from (L. 91).
1- n-heptane (C_7H_{16}) and density of the liquid; 2- $C_{14}H_{30}$; 3- $C_{10}H_{22}$; 4- C_7H_{16}; 5- C_6H_{14}.

In reference (L. 21) when the voltage was turned on the surface of the mercury cathode did not remain in fixed position, and in determining E_{br} it was necessary to introduce corrections. This situation for such small distances between electrodes undoubtedly reduced the accuracy of the measurements.

The temperature dependence of breakdown voltage for liquid hydrocarbons of the paraffin series may, according to the data of reference (L. 91), be represented by the following formula:

$$E_{np} = C_1 e^{C_2/T}, \tag{20}$$

where C_1 and C_2 are constants; of these C_2 does not depend on the electrode material but C_1 rises with an increase in the work function of electrons from the cathode.

Apparently this formula is appropriate only for very small spark gaps and short pulses. Experiments with wider gaps showed that the temperature trend of the reduction in E_{br} is found to be somewhat different.

But with DC voltage and very small distances between electrodes l the regularity of the drop in E_{br}, as may be traced from the curves of Fig. 6, become more complicated.

The curves of Fig. 55 were obtained for breakdown of the same hydrocarbon liquids of the paraffin series, but the distance between the spherical electrodes made of stainless steel were increased up to 200 microns. The duration of the rectangular pulses equalled 4.5 microseconds. A pulse generator at a voltage of 75 kv was assembled to the multiplication circuit of reference (L. 56),

The liquids under study were distilled several times and filtered through a filter made of sintered glass with pores smaller than 1 micron. In order to remove moisture these liquids had lain in contact with silica gel for several weeks. The portions of the liquids to be studied were subjected to breakdown only once. The carefully treated electrodes used in this experiment were also used only one time. In Fig. 55 the dotted line touching curve 1 denotes the freezing point, and the lines touching 2 and 3 the boiling points.

In curve 1 (Fig. 55) for n-decane a relatively flat section of the variation of E_{br} may be noted in the temperature range from 15 to 45° C. Such regions in Fig. 54 for the same n-decane are absent. In addition to the influence of the spark gap width, a reason of this lack of correspondence might be found in the non-uniform state of the electrode surface in breakdowns and the varying methods for purifying the liquids.

On the other hand with DC voltage with however a spark gap measured in fractions of a millimeter a sharper drop in values of E_{br} was registered for hexane (see Fig. 56). Here the dotted lines also denote the boiling point (L. 65).

According to reference (L. 56), when the voltage is switched into the interelectrode gap microscopic gas bubbles are formed. The surface tension for these bubbles decreases with a rise in temperature, but the vapor pressure inside increases. This situation creates favorable conditions for drawing out the bubbles along the lines of force of the applied field. For some critical distance of removal of these bubbles one from the other the process of shock ionization begins and the dielectric breaks down.

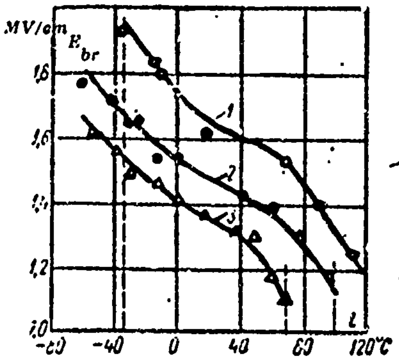


Fig. 55. Dependence of E_{br} of liquid hydrocarbons on temperature. 1- $C_{10}H_{22}$; 2- C_7H_{16}; 3- C_6H_{14}.

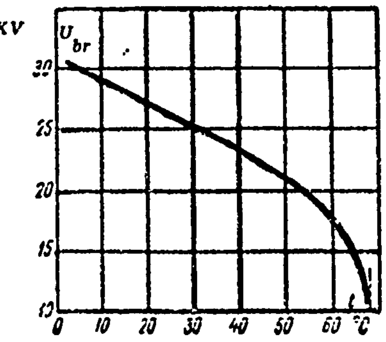


Fig. 56. Dependence of U_{br} of hexane on temperature for DC voltage and normal pressure.

The authors of reference (L. 56) believe that the longer the chain of molecules in the hydrocarbon liquids of the paraffin series, the greater the surface tension and the less is the vapor pressure within the bubbles. In order to draw them out along the field it is necessary to apply more voltage. Therefore the breakdown voltage for an increase in density becomes higher.

In article 1-3 analogous curves of the temperature dependence of E_{br} were run, but they were obtained with DC voltage. From a comparison of Figs. 6,54 and 55 on may conclude that for pulse voltage the effect of structural factors is not expressed so fully. However this conclusion, apparently, cannot be extended to a silico-organic liquid, whose breakdown voltage with DC voltage and with $l = 4 \times 10^{-3}$m drops smoothly (see curve 1, Fig. 57). In principle there is only a certain type of similarity with the temperature trend of hydrocarbon liquids (curves 2 & 3) and it is possible to isolate only one particular inflexion point for $t = 75^0$ C, and not two, as in Fig. 6.

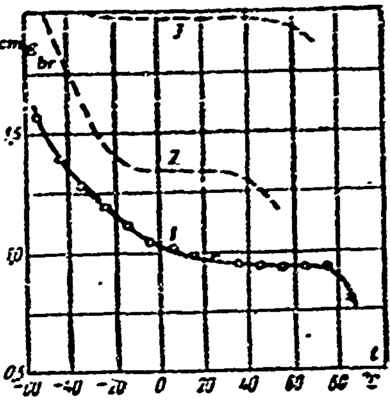


Fig. 57. Dependence of E_{br} on temperature for insulating liquids. 1- silicone dimer; 2- n-hexane; 3- n-decane.

The temperature maximum of U_{br} for post voltage is found also for such a highly polar liquid as distilled water, but with a sharply inhomogeneous electric field (see Fig. 58). It is interesting to note that the values for the dielectric constant of water for a rise in temperature decrease noticeably (L. 114). For such sharply inhomogenous electric fields the effect of polarity is established for water (L. 103). As in the case of the breakdown of air gaps, U_{br} of water is significantly higher for a positive point in plane than for the opposite polarity for the point.

Interesting data on the variations of values of E_{br} for transitions of sulphur from the solid into liquid and afterwards into the gaseous state (between -200 and 1000^0 C) have been obtained in references (L. 114 and 115).

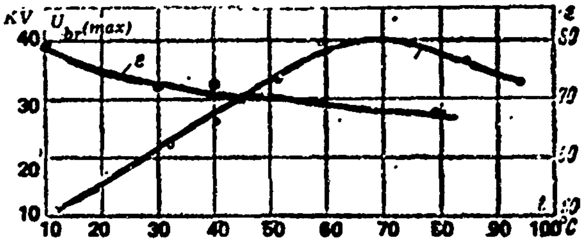


Fig. 58. Dependence of U_{br} and the dielectric constant of distilled water on temperature.

4-2. The Influence of the Applied Voltage Frequency

The dependence of E_{br} of liquids on the frequency of the applied voltage is a subject of great interest in practice. As an example we may point out that high voltage field condensers with duralumin plates, filled with clear transformer oil having very high purity (purified with 30% concentrated H_2SO_4), may operate in high voltage smelting furnace circuits for several years when the working voltage is E = 3 kv/cm at a frequency of f = 2 x 10^5 hz.

In other countries an insulating liquid which goes by the name of "Electronol" is recommended for such condensers with aluminum plates. It is obtained from dibutyl ether and sebacic acid $[C_8H_{16}(COOC_4H_9)_2]$. This liquid is colorless. Some electrical and physical properties of this liquid follow (L. 49 & 116):

Specific gravity	0.94 g/cm³
Solidification temperature	-10°C
Ignition temperature	170°C
Viscosity at 38°C	6 centistokes
Breakdown voltage at 58 hz and 1 > 1 mm	0.14 - 0.16 mv/cm
Dielectric constant at 25°C	4.4
Dielectric loss angle tangent at 10 khz in the temperature range 30 - 100°C	$<1.5 \cdot 10^{-4}$

The dependence of the breakdown voltage of this liquid on the distance between plane electrodes in the capacitors at a frequency of 500 khz is the same as for transformer oil. Lectronol absorbs a relatively large amount of water, but for it the reduction in E_{br} is much less than for transformer oil, with the same degree of humidification.

At a frequency of 500 khz the breakdown voltage of lectronol decreases by approximately 60%.

It was mentioned above that for exposures less than from 1 to 2×10^{-6} seconds the values of E_{br} of the liquids increase. Therefore for frequencies of 10^6 hz one would expect a rise in E_{br} if there were no influence from other factors facilitating the drop in E_{br}, for instance, the generation of heat from dielectric loses. In the case of cold emission of electrons and their capture by molecules of the liquid, bulk negative charges may form at the cathode, and with a change in polarity the "former" cathode the field intensity may rise drastically and breakdown may occur.

In references (L.85 & 117) such breakdowns experienced in turpentine, transformer oil and paraffin oil at frequencies 50 and 3.2×10^4 hz are reported. An especially unique dependence of U_{br} on frequency and interelectrode distance 1 is revealed for turpentine. If we designated the breakdown voltages at frequencies 50 hz and 3.2×10^4 hz respectively by U_{br}' and U_{br}'', then for 1 less than 3 mm the magnitude of U_{br}'' is greater than that of U_{br}', but for 1 greater than 3 mm, on the contrary, U_{br}'' is less than U_{br}'. And in the case of 1 = 3 mm the breakdown voltages are the same.

For a distorted wave form of a sinusoidal AC voltage of 50 hz (sharp peaks) the breakdown voltages of some liquids are higher than with flat peaks. This difference in U_{br} is manifested in some tens of breakdowns in one single liquid (L. 118 - 121).

For transformer oil when the frequency is increased up to 800 hz and 1 is held fixed the values of E_{br} rise. The corresponding data are presented in Table 21 for two kinds of oils having differing degree of purification (A & B).

Table 21. Values of the breakdown voltage for transformer oils.

Frequency, hz	Breakdown Voltage mV (max)		Frequency, hz	Breakdown Voltage mV (max)	
	A	B		A	B
0	0.025	-	150	0.430	0.540
25	0.340	-	225	0.470	0.570
50	0.380	0.480	800	-	0.610

But on the other hand for frequencies greater than 800 hz a drop in E_{br} takes place (L. 122). We may follow such a regularity in the curves of Fig. 59 which is also for transformer oil. In this same figure the dielectric loses (tg δ) are indicated by means of Fig. 4. They rise continuously with an increase in frequency, a fact which is important with respect to the transition to a electrical form of breakdown to the thermal form.

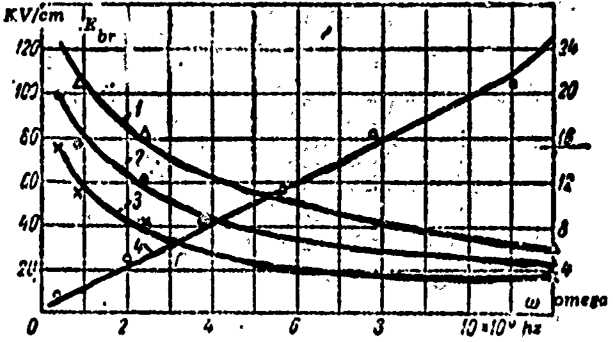


Fig. 59. Dependence of E_{br} and tg δ of transformer oil on frequency of applied voltage. 1- distance between spherical electrodes 1 = 1 mm; 2- 1 = 2 mm; 3- 1 = 4 mm; 4- values of tg δ.

The variations in breakdown voltages for transformer oil and xylene with various distances between the electrodes and frequencies in the range from 4 x 10^5 to 1.2 x 10^7 hz are represented by curves in Figs. 60 and 61. Here the same regularity is recognized in the dependence $E_{br} = \Psi (1)$ as was seen in Fig. 59: for a fixed frequency and an increase in 1 the values of E_{br} decrease. For $f = 10^7$hz the breakdown voltage already has little dependence on the interelectrode distance (L. 85 & 122).

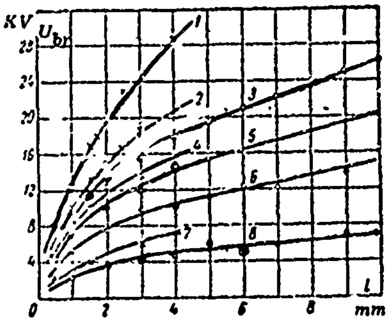


Fig. 60. Dependence of U_{br} of transformer oil on interelectrode distance for various frequencies. 1- sphere-sphere, f=4.0 x 10^5hz; 2- same, but f=8.6 x 10^5hz; 3- point-sphere, f=4.5 x 10^5hz; 4- sphere-sphere, f=2.4 mhz; 5- point-sphere, f=8,6 x 10^5hz; 6- same, but f=2.4 mhz; 7- sphere-sphere, f=12 mhz; 8- point-sphere, f=12 mhz.

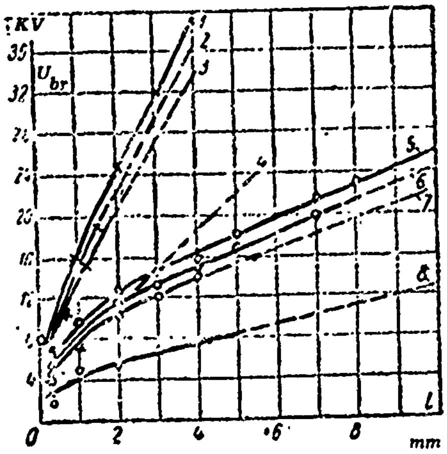


Fig. 61. Dependence of U_{br} of xylene on interelectrode distance for various frequencies. 1- sphere-sphere, f=4 x 10^5hz; 2- same, but f=8.6 x 10^5hz; 3- same, but f=2.4 mhz; 4- same, but f=12 mhz; 5- point-sphere, f=4 x 10^5hz; 6- same, but f=8.6 x 10^5hz; 7- same, but f=2.4 mhz; 7- same, but f=2.4 mhz; 8- same, but f=12mhz

Interesting regularities were discovered in an investigation of transformer oil and xylene in the temperature range from -10 to 148° C. Breakdown was produced in a gap of 1 = 1 mm between spherical electrodes. The frequency was varied within the limits 4 x 10^5 - 1.2 x 10^7 hz. The curves opbtained are presented in Fig. 62 (L.85). They have a temperature maximum which shifts into the region of higher temperatures as the frequency is increased. But the maximum values of E_{br} decrease in the process. Numerical data, referring to these maxima, are corrected in Table 22.

One may hypothesize that for specified temperatures and frequencies the electrical form of breakdown passes over to the thermal form.

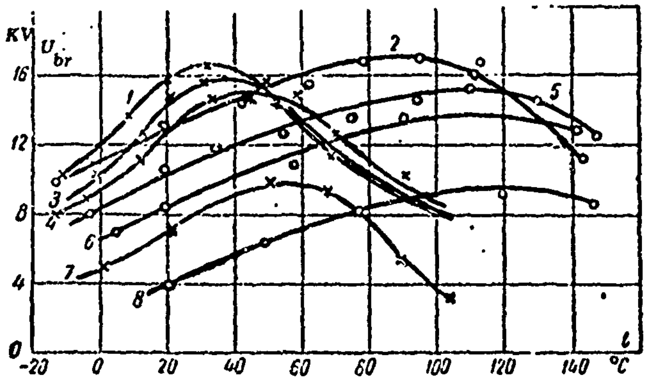


Fig. 62. Dependence of U_{br} of xylene and transformer oil on temperature for various frequencies. 1,3,4,5 xylene; 2,5,6,8 - transformer oil; 1 and 2 - $f=4 \times 10^5$ hz; 3 and 5 - $f=8.6 \times 10^5$hz; 4 and 6 - f=2.4 mhz; 7 and 8 - f= 12 mhz.

The dielectric loses in a unit of volume of the liquid are equal to:

$$W = \frac{\omega\varepsilon}{4\pi\cdot 9\cdot 10^{11}} \quad (21)$$

$$\mathrm{tg}\delta E^2 \ [\mathrm{watt/cm^3}]$$

These depend on temperature to the extent that the dielectric loss coefficient ε tg δ depends on temperature.

The existence of two relaxation maxima for the loss angle tangent is considered possible - a low temperature and a high temperature maximum (L. 85). When the frequency is increased E_{br} is reduced. Consequently, the losses may rise owing to an increase in ω and may fall owing to a decrease in E. But the efficiency of the convective extraction of heat from the interelectrode gap to the upper layers of the liquid depends on the liquid's viscosity and the latter depends on temperature. This whole set of dependences in the complicated process of heat generation and heat extraction, and also the possible effect of space charges on the emission of electrons from the cathode, underlies the occurrence of maxima in E_{br} and their shift in the direction of higer temperatures. A more complete and satisfying explanation for this regularity has meanwhile not been found.

Table 22. Maxima in the breakdown voltages of transformer oil and zylene for various frequencies.

Liquid	Frequency Hz	Temperature at maximum, centigrade	Maximum value of E_{br}, kv/cm
Xylene	$4 \cdot 10^5$	32	168
same	$8,6 \cdot 10^5$	38	159
same	$2,4 \cdot 10^6$	48	150
same	$1,2 \cdot 10^7$	58	105
Transformer oil	$4,0 \cdot 10^5$	90	175
same	$8,6 \cdot 10^5$	110	150
same	$2,1 \cdot 10^6$	120	136
same	$1,2 \cdot 10^7$	122	99

Some other dependences of U_{br} = psi (1,t) were discovered for polar liquids of electrodes consisting of a point and a plane. It turned out that for frequencies up to 7 x 10^6 hz the breakdown voltage of, for instance, nitrobenzene and water has practically no dependence on temperature. A reduction in U_{br} is observed only at temperatures close to the boiling temperature (L. 123). At a frequency of 7 x 10^6 hz and higher a monotonic decrease in U_{br} is observed. For mixtures of two liquids, however, the breakdown voltage maxima are fixed for specified frequencies.

As the viscosity of methylpolysiloxane, phenolethanolamine, dicholorobenzene and others is reduced at low frequencies the values of U_{br} rise, but for high frequencies they decrease (L. 123). Such a dependence is found also for electrodes consisting of a sphere and a plane. The increase in U_{br} for low frequencies is explained by the more efficient extraction of heat, but the decrease in U_{br} at high frequencies is explained by the unfavorable conditions for the attachment of electrons to molecules of the liquids.

The breakdown voltage of transformer oil at high frequencies also turns out to be dependent on external pressure, as is seen from the curves of Fig. 63. Breakdown was produced in gap of 1 = 5.6 mm between spherical electrodes, and also between a point and a sphere. As the frequency is raised the rate of growth of U_{br} equals psi (P) slows down, and for f = 1.2 x 10^7 hz the breakdown voltage has practically no dependence on pressure.

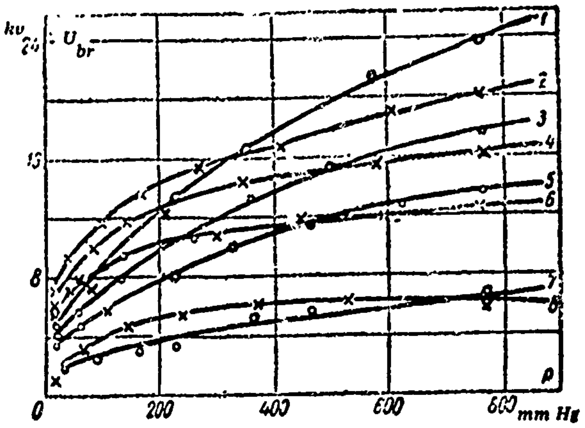


Fig. 63. Dependence of U_{br} of transformer oil on external pressure at various frequencies. 1- sphere-sphere, f = $4 \cdot 10^5$ hz; 2- point-sphere, f = $4 \cdot 10^5$ hz; 3- sphere-sphere, f = $8 \cdot 10^5$ hz; 4- point-sphere, f = $8 \cdot 10^5$ hz; 5- sphere-sphere, f = 2.4 mhz; 6- point-sphere, f = 2.4 mhz; 7- sphere-sphere, f = 12 mhz; 8- point-sphere, f = 12 mhz.

Here, in addition to the evolution of a large amount of heat, a rather significant role is still played by ionization processes in the gas bubbles. At high frequencies, as was the case for short rectangular pulses, various types of impurities, contamination, and humidification do not exert a large influence on U_{br}. The corresponding numerical data are reported in Table 23.

Table 23. Breakdown voltages (kv) for transformer oil having various degrees of purification.

Frequency, hz	Manufactured Oil	Humidified Oil	Filtered Oil with 2% Butyric Acid Added	Filtered Oil	Filtered Oil and Dryed Oil
50	<100	<100	<160	250	310
$4 \cdot 10^5$	66	<65	71	83	85

From the table it follows that at a frequency of 50 hz filtering and drying of transformer oil may be employed to raise U_{br} by more than a factor of 3, but a frequency of 4×10^5 hz - only by 13%.

4-3. The Effect of the Electrode Material

It has long been observed that the state of the electrode surface exerts a definite influence on the size of E_{br} for liquid dielectrics. Contamination and oxidation of these surfaces, and also an insufficient degassing and a poor polishing job, usually depress E_{br} (L. 62, 64, 96 and 124).

In reference (L. 62) E_{br} was determined for ligroin, hexane, and xylene using electrodes made of various metals. The experiments were carried out with an AC voltage at 50 hz. Comparatively large spark gaps were caused to break down. The results obtained are presented in Table 24.

Table 24. Values of breakdown voltage (mv/cm) of liquid dielectrics for electrodes made of various metals.

Liquids	Iron	Yellow Copper (Brass)	Lead	Copper	Aluminum	Gold	Zinc	Silver
Ligroin	0.400	0.420	0.435	0.455	0.450	--	0.490	--
Hexane	0.355	0.370	0.380	0.435	0.440	0.430	0.475	0.480
Zylene	0.430	0.410	0.465	0.470	0.480	0.485	0.515	0.535

The data in Table 24 are arranged in order of increasing E_{br} for each liquid under investigation. The few exceptions are comprised of only the values of E_{br} for benzene with electrodes of copper and aluminum; for hexane with electrodes of aluminum and gold; of xylene with electrodes of iron and brass.

For the rise in E_{br} it is possible to write the following inequality:

$$Fe < Pb < Cu < Al < Zn < Ag.$$

Inasmuch as the thermal conductivity of the metals rises in approximately the same sequence, the conclusion was reached that the extraction of heat from the interelectrode gap has an effect on E_{br}.

From the values of E_{br} of the liquids under examination we may conclude that they were not very well purified and with increased electrical conductivity they were able to break down as a result of thermal instability. Therefore the reported series of inequalities may apparently be considered typical only for poorly purified liquid dielectrics.

For breakdown in gaps of l = from 1 to 10^{-3} cm between a negative point in a plane, the gaps being filled with highly purified n-hexane, no influence from the electrode material was detected. The experiments were conducted with DC voltage and with electrodes made of Cr, Cu and Al (L. 125). Some influence was noted only for the negative plane. This observation was explained in reference (L. 126) by saying that the emission of electrons from the points was sufficiently intense for any metal. But it is possible to detect its effect on E_{br} of liquids only in the case where the electrode surface is cleaned carefully, degassed and polished and where the emission power of the cathode is not very great. These conditions are satisfied by the negative planes made of Cr, Cu and Al.

The same effect is noted for transformer oil with pulses with a rise-time of 1 microsecond and a wave length of 3 microseconds (L. 127).

Reports on the influence of electrode material on E_{br} for transformer oil and n-hexane for a spherical electrode shape and with DC voltage appear in references (L. 100 & 128).

For the experiments with n-hexane iron, copper and aluminum spheres were shaped or turned from solid pieces of the metals, and the chromium, platinum, nickel, and silver spheres were fabricated by depositing these metals on brass by an electrolytic means (L. 100). The liquid was thoroughly purified. The discharge currents were limited with an ohmic resistor of value 18 megohmns.

The measured values for E_{br} of un-degassed electrodes of chromium and silver are shown in the form of stepped curves in Fig. 64. Along the axis of the abscissa is plotted the number of breakdowns following one upon the other. The small increase in values of E_{br} in article 3-1 is explained by the degassing of electrodes with an electrical spark. If they are carefully polished, cleaned and degassed, then such an increase in E_{br} is not observed. Consequently in the given case, only the treatment of the electrode surfaces, and infact mainly the cathode surface (condition process), has a telling effect. This effect does not depend on the liquid being studied. Information on the effect of polishing the electrodes on E_{br} appears in reference (L. 129).

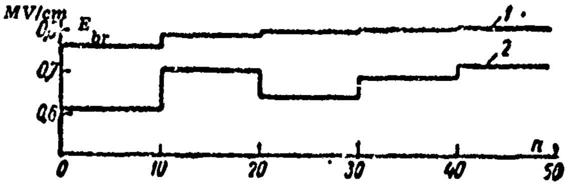


Fig. 64. Effect of electrode material on E_{br} for hexane. 1- electrodes of chromium; 2- electrodes of silver.

Values of E_{br} for un-degassed n-hexane and for un-degassed electrodes of various materials are presented in Table 25 (L. 86). Here also are shown data on the electron work-function in vacuum from un-degassed metals (cathodes) (L. 130 & 131).

Table 25. Breakdown voltage of n-hexane.

Electrode Metal	Breakdown Voltage, mV/cm			Electron Work Function From Un-degassed Metals, ev
	Mean	Minimum	Maximum	
Chromium	0.791	0.584	0.952	--
Iron	0.853	0.486	0.993	3.02
Silver	0.676	0.486	0.912	3.09
Copper	0.814	0.527	0.972	3.89
Platinum	0.737	0.560	0.872	3.63
Nickel	0.873	0.592	1.012	3.68
Aluminum	0.756	0.576	0.992	1.77

Note: Liquid and electrodes not de-gassed.

According to the mean values of E_{br} in this table, one may construct a new inequality:

$$Ag < Pt < Al < Cr < Cu < Fe < Ni$$

This does not coincide with the sequence in the inequality for electron work-function in vacuum from un-degassed metals. For platinum and nickel the work-function is almost identical. But the breakdown voltage of n-hexane with electrodes of nickel is significantly larger. With aluminum which has the smallest work-function the values of E_{br} for n-hexane were found to be by no means the smallest. Therefore, we may conclude that there is no correlation at all between the quantities being compared.

For n-hexane which has been degassed and distilled many times and with cleaned and degassed electrodes somewhat differing data are obtained; they are shown in Table 26.

Judging from these data the influence of the electrode material on E_{br} for n-hexane is not large. The inequality derived from the growth in values of E_{br} for this case would be as follows:

$$Cu < Ag < Fe < Cr$$

A significant effect of electrode material has been established for breakdowns in very thoroughly purified transformer oil in reference (L. 37). The greatest effect with regard to the increase in E_{br} for oil was attained by passing it through a filter with pores of diameters smaller than 1 micron.

The experimental values of E_{br} for DC voltage and 1 = 100 microns are reported in Table 27.

Table 26. Breakdown voltage for n-hexane

Electrode Metal	Breakdown Voltage, mV/cm		
	Mean	Minimum	Maximum
Chromium	0.899	0.673	1.093
Iron	0.872	0.754	0.952
Silver	0.826	0.576	1.016
Copper	0.823	0.576	0.972

According to the data of Table 27, when transformer oil is saturated with air, its E_{br} is reduced sharply. However, small additions of air produce the opposite effect. The greatest value of E_{br} was observed when using electrodes of stainless steel.

Table 27. Effect of electrode material on the breakdown voltage of transformer oil

Electrode Material	Breakdown Voltage mV/cm
Stainless Steel	1.025
Chromium	0.865
Steel	0.890
Copper	0.886
Aluminum	0.880
Stainless Steel (oil saturated with air at 760 mm Hg)	0.670
Aluminum (oil also saturated with air)	0.570

In order to elucidate the effect of the cathode and anode material, breakdowns were produced in oil with electrodes made of various metals. If the air content in the oil was small, then in all cases the cathode material exerted an influence on E_{br}. But when the oil was saturated with air the anode had the most prominent effect.

According to the report (L. 132), the breakdown voltage of heptane and ligroin may be raised by a factor of 2 or more by means of a fine polishing of the electrode surfaces and a thorough degassing of the same. From data on the influence of the degree of oxidation of the cathode on the electrical strength of transformer oil are presented in reference (L. 133).

From the statements made above we may form the conclusion that the material of the electrodes has an effect on the E_{br} of different liquid dielectrics. But how then do we explain the differences of opinion which occur in the conclusions formed by various authors concerning the regularities of this effect? It is possible to suppose that one of the principal reasons is lack of uniformity in the state of the elctrode surfaces. We have already mentioned above the effect of treatment of their surfaces. Moreover, as it turned out that in conjunction with the electrode material, the liquid under examination, and also the interelectrode gap-width have a very definite effect. According to the data of reference (L. 99), as l increases the effect of electrode material is reduced, and for large l (several millimeters) it ceases entirely.

Reports on the joint effect of the nature of the insulating liquids and the electrode material appear in reference (L. 42). The experiments were carried out with compressed gasses: argon, oxygen and nitrogen. They serve as good objects for study, since they are the most simple of all the liquid dielectrics. Regardless of the fact that they have no particular practical value for the purpose of electrical insulation, they have a series of valuable properties. For example, compressed argon is inert, does not react with metal electrodes and does not capture free electrons (L 134 & 135). Diatomic oxygen, on the other hand, efficiently captures electrons and forms negative ions of small mobility. Furthermore, it enters into an interaction with the surface layers of the electrode metal and may form oxide films.

In the experiments of reference (L. 42) breakdown was produced in gaps of from 20 to 100 microns between spheres immediately after breakdown with DC voltage the spark gap was shunted with a thyratron and the discharge came to an end. Therefore the formation gaseous products in the breakdowns were held to a minimum. The results obtained are shown in Table 28.

Table 28. Average values of the breakdown voltage with electrodes of various materials

Electrode Material	Electron Work Function in Vacuum, ev	Breakdown Voltage, mV/cm		
		Liquid Argon	Liquid Oxygen	Liquid Nitrogen
Stainless Steel	--	1.40	2.38	1.88
Brass	--	1.01	1.44	1.62
Copper	4.47	1.40	1.81	--
Gold	4.58	1.16	1.24	1.50
Platinum	5.29	1.10	2.00	2.24

From the data of Table 28 it is also possible to form conclusions on the absence of correlation between the values of E_{br} and the work-function of electrons from the cathode into vacuum. For the liquids that were investigated the following qualities were obtained:

Compressed gases	Inequalities
Argon	Cu + Zn < Pt < Au < Cu < Fe°
Oxygen	Au < Cu + Zn < Cu < Pt < Fe°
Nitrogen	Au < Cu + Zn < Fe°< Pt

Here as is conventionally denoted by Cu + Zn, and stainless steil by -Fe^0. It is clear from the column of inequalities that E_{br} for compressed gases depends, in fact, not only on the material of the electrodes but also on the physical and chemical properties of the liquids being studied. This joint effect comes about because of the oxide insulating films on both the cathode and on the anode.

Concerning the effect of these films on E_{br} for liquid argon of purity 99.95% with small admixtures of nitrogen, oxygen, and hydrogen, information is given in reference (L. 43). A portion of the experiments was conducted with spectroscopically pure liquid. The electrodes of various materials were placed into a medium of dry air for oxidation over a specified period of time immediately following polishing. Portions of the liquid experienced breakdown only once and always with fresly prepared electrodes. The distance between them was varied within the limits 2 x 10^{-3} to 10^{-2} cm.

In Fig. 65 experimental curves of E_{br} for liquid argon as a function of the degree of oxidation of the electrodes made from various materials are presented. Along the axis of the abscissa the oxidation time is plotted in minutes. The degree of oxidation was according to convention evaluated from the duration of time over which the electrodes were immersed in the dry air medium.

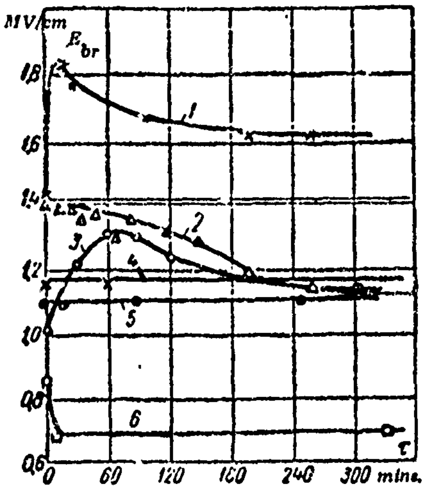


Fig. 65. Breakdown voltage of liquid argon as a function of degree of oxidation of electrodes made of: 1- stainless steel; 2- copper; 3- brass; 4- gold; 5- platinum; 6- aluminum.

For unoxidized electrodes of gold and platinum the values of E_{br} did not depend on the duration of oxidation (curves 4 & 5). The occurrence of a maximum in E_{br} was observed for electrodes made of stainless steel and brass. A curve which sharply differed from the others was obtained for electrodes of aluminum. After oxidation of these electrodes over the course of several minutes the values of E_{br} dropped sharply and remained constant for the subsequent longer oxidation.

In order to bring out the separate effect of the cathode and anode, they were fabricated out of different metals, as also in the experiments of reference (L. 37). Oxidation took place also in a medium of dry air. Data on the electrode material, their oxidation time and the values of E_{br} are reported in Table 29.

Based on these data one may conclude that only the surface state of the cathode can be considered to be absolutely non-decisive. When an aluminum (oxidized) anode is replaced with an oxidized anode of stainless steel (see Table 29) and the cathode remains unchanged, E_{br} of liquid argon increased by a factor of more than 2 (0.69 and 1.44 mv/cm). The same exchange of cathode metal when the anode of aluminum was unchanged permitted E_{br} to be raised by only 27% altogether (0.69 and 0.88 mv/cm). From Table 29 it is also seen that oxidation of the stainless steel cathode only exerts a small influence on the value of E_{br}, if the anode is not oxidized (made of gold).

Table 29. Effect of electrode material on the breakdown voltage of liquid argon.

Cathode Material	Oxidation Time, min.	Anode Material	Oxidation Time, min.	Breakdown Voltage mV/cm
Aluminum	15	Aluminum	15	0.69
"	15	Stainless Steel	15	1.44
Stainless Steel	15	Aluminum	15	0.88
"	15	Stainless Steel	15	1.86
"	0	Gold	--	1.22
"	17	"	--	1.26

The effect of separate oxidation of the anode and cathode on E_{br} of the same liquid argon is illustrated by the curves in Fig. 66. For an unoxidized anode E_{br} for the cathode rises as the cathode is oxidized. In this case the emission of electrons from the cathode is an influential factor. When the thickness of the oxide film is increased the intensity of emission goes down and E_{br}

rises (curve 1). On the other hand, as the degree of oxidation of the anode goes up with the cathode (of gold) unoxidized, E_{br} decreases (curve 2). The mechanism of this decrease would not be completely clear if we did not make the assumption that an insulating or semi-conducting film existed on the surface of the gold cathode. Electrons, emitted from the cathode, are captured by impurity molecules of oxygen and form negative ions. As they approach the oxide film on the anode they increase the field intensity until shock ionization occurs. The positive ions which are formed in the process move to the cathode and, collecting at the oxide film, also enhance the field intensity. The emission of electrons is thereby reinforced and E_{br} decreases. Without such a film at the cathode there would not be any reasons for E_{br} to fall. This is corroborated, for instance, by the behavior of an oxide cathode and a stainless steel anode described in Fig. 66 (curve 3).

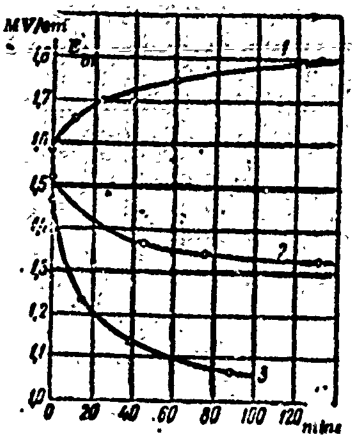


Fig. 66. Effect of the degree of separate oxidation of cathode and anode on E_{br} for liquid argon. 1- both electrodes of stainless steel, but cathode with varying degree of oxidation and anode not oxidized; 2- cathode of gold and anode of stainless steel with varying degree of oxidation; 3- both electrodes of stainless steel, but cathode oxidized over a period of 24 hours and anode with varying degree oxidation.

The appearance of a maximum for E_{br} in Fig. 65 may be explained by the fact that with slight oxidation of the anode negative ions do not collect at its surface, but they are neutralized in touching the anode. The value of E_{br} is then determined only by the emission of electrons from the cathode. As the thickness of the oxide film is increased the emission becomes weaker and E_{br} rises. But a fall in E_{br} begins only in the case where an insulating film is forming on the surface of the anode.

The sharp drop in E_{br} of liquid argon (curve 6, Fig. 65) is explained by the very fast oxidation of aluminum. An insulating film on the surface of such electrodes is formed almost immediately, as soon as they come into contact with air.

The effect of anode treatment on the value of breakdown voltage for n-hexane was observed also for pulsed voltage (L. 136). For a surface of this electrode which was not very smooth E_{br} dropped by about 9%.

It was mentioned before that for DC voltage there exists no correlation between the electron work-function in vacuum and the variation in E_{br} for liquid dielectrics. This is undoubtedly a consequence of the strong influence that the state of the cathode surface has on the emission of electrons, and with sufficient tiem for the ions to travel between the elecyrodes - also a consequence of the influence of the oxidized anode. For pulsed voltage the emission of electrons must be determined only by the condition of the cathode surface. If we carry out experiments with unoxidized cathodes made of various materials, then for short pulses it would be possible, and one would succede, in establishing such a correlation. According to one report (L. 91), this was actually established for breakdowns of carefully purified n-hexane and methyl alcohol (Fig. 67). Here the work-function of electrons in vacuum is plotted along the axis of the abscissa. There is some doubt to be attached to these experiments, but only as a result of the fact that un-degassed electrodes were employed.

It is important to note that the dependence of E_{br} on electrode material is expressed also in the breakdowns of certain solid dielectrics (L. 137-139), and even in the growth of dendrites in crystals of rock salt (L. 140).

4-4. The Role of Cold Emission of Electrons from the Cathode

On the basis of statements made in the preceeding paragraph we may arrive at the conclusion that, all things considered, the effect of elctrode material on E_{br} of liquid dielectrics is realized through the emission of electrons from the cathode, although this emission was considered only qualitatively. In the present paragraph quantitative data on this phenomenon will be presented as well.

In thoroughly purified n-hexane with DC voltage and various distances between flat polished electrodes of steel and phosphor bronze, the current density turned out to be a function of both the material of the electrodes and of the distance 1 between them (Fig. 68). The current was measured with the aid of an electrometer. In places where leakage might occur, guard rings of gold were used (L. 91). The purification of n-hexane to be examined was discussed in in §3-4.

For small field intensities the measured current density may be expressed by the formula $J = J_0 e^{\alpha 1}$ where is the ionization coefficient in the Townsend theory. From this it necessarily follows that the emission current from the cathode is increased by the shock ionization mechanism. The coefficient α depends on the field intensity. For air (L.65,141,142) for instance, α is about equal $c(E - E_0)^2$, and for some liquids it is equal to $c^1(E - E_0'$

Extrapolation of the curves of Fig. 68 to 1 = 0 gives the current density at the cathode J_k. Its dependence on E turned out to be the same as in the Fowler and Nordheim formula for the cold emission of electrons (L. 143):

$$J_{\kappa} = aE_{\kappa}^2 e^{-b/E_{\kappa}}, \qquad (22)$$

where E_k is the field intensity at the cathode; a and b are constants depending on the work-function ϕ of electrons from the metal into vacuum in which a is about equal to $1/\phi$ and b is about equal to phi to the power 3/2.

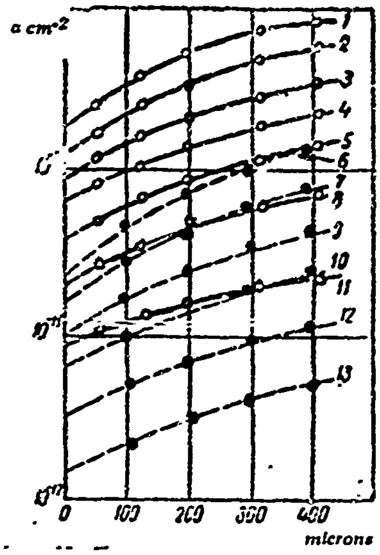


Fig. 68. Current density for highly purified n-hexane as a function of the interelectrode gap width l for various E. 1-electrodes of phosphor bronze, E=0.22 mv/cm; 2- same, but E=0.2 mv/cm; 3- same, but E=0.18 mv/cm; 4- same, but E=0.16 mv/cm; 5- same, but E=0.14 mv/cm; 6- electrodes of steel, E=0.2 mv/cm; 7- same, but E=0.18 mv/cm; 8- electrodes of phosphor bronze, E=0.12 mv/cm; 9- electrodes of steel, E=0.15 mv/cm; 10- same, but E=0.14 mv/cm; 11- electrodes of phosphor bronze, E=0.10 mv/cm; 12- electrodes of steel, E=0.12 mv/cm; 13- same, but E= 0.10 mv/cm.

The discharge of electrons into the dielectric medium is effected, as noted above, with a significantly smaller expenditure of energy.

Formula (22) may be considered valid only for the temperature of absolute zero. As soon as there is a measurable rise in temperature, thermal emission must also occur. In the case of large field intensities a drop in the potential barrier for the discharge of electrons (Schotky effect) takes place (L. 144). The applicability of the Fowler and Nordheim equation for the discharge of electrons into vacuum is confirmed in references (L. 145 & 146). According to reference (L. 91), the experimental points for J_k are distributed on a straight line in the coordinates log (J_k/e^2) and

1/E, but the values of the coefficient a and b diverge widely from the theoretical values (Table 30).

Table 30. Experimental and theoretical values of the coefficients a and b in formula (22).

Cathode Material & Discharge of Electrons	a,a/cm^2	b,v/cm
Phosphor Bronze, Discharge into n-hexane (from experiment)	$2.76 \cdot 10^{-20}$	$2.6 \cdot 10^5$
Steel, Discharge into n-hexane (from experiment)	$5.1 \cdot 10^{-21}$	$2.66 \cdot 10^5$
Metal with work function phi in vacuum (from theory	$1.55 \cdot 10^{-6}\ \phi^{-1}$	$6.8 \cdot 10^7\ \phi^{3/2}$

The work function phi is usually equal to several electron volts, and the values of the constants for n-hexane and vacuum differ by several orders of magnitude. Apparently, equation (22) is not wholly suitable for the emission of electrons from the cathode in n-hexane, even though a linear dependence is obtained in the indicated coordinates.

In the preceeding paragraph it was reported that, in addition to the field intensity and work-function, the surface condition of the electrodes exerts a strong influence on the emission of electrons, and this condition is not taken into account in formula (22).

The poor applicability of this formula for the emission current in the same hexane was demonstrated also with experiments (L. 147). The liquid contained 99 mole percent of n-hexane and the most probable impurity which was methylcyclopentane. This hexane was not subjected to chemical treatment, but was thoroughly purified, distilled, and dried. Moreover, the liquid underwent electrical purification. Measurements of current for DC voltage was carried out also with the aid of an electrometer. For electrodes a sphere and plane were used.

When the DC voltage is turned on the currents flowing through the liquid ordinarily fall (sometimes over several orders of magnitude) during the first ten or twenty seconds, and then, in approximately one minute, adjust themselves and again show almost no variation for several hours following. In the experiments which were analyzed the current measurements were conducted within one minute after the voltage was turned on.

Even with thoroughly clean electrodes of various metals the shape of the I-V curves appeared not to be uniform. Their slope with respect to the coordinate axes is different (see Fig. 69). On this basis the conclusion was reached that the Fowler and Nordheim equation (22) for cold emission of electrons in n-hexane is not applicable. In the same way the equation for thermal emission turned out not to apply:

$$J = AT^2 \dot{D} e^{-(\Xi - E')/kT}. \qquad (23)$$

Current measurements in reference (L. 147) were performed for electrodes made of stainless steel, nickel, gold and copper. For the work-function of electrons from these metals into vacuum one may write the inequality

$$\mathrm{Fe}^0 < \mathrm{Ni} < \mathrm{Au} < \mathrm{Cu}.$$

The size of the currents in n-hexane for electrodes of these metals and with other conditions identical would have to vary in the same sequence. But in reality, as is seen from the curves of Fig. 69, the sequence obtained was somewhat different. Based on this, the author of reference (L. 147) also came to the conclusion that the determining factor in emission is not the material of the electrodes, and therefore also not the work-function of electrons into vacuum, but it is the thin insulating layer on the surface of the cathode. At this location the positive ions which are always present in the liquid may accumulate; these ions increase the field intensity and consequently also enhance the emission of electrons. The indicated hypothesis has been confirmed in the experiments of other authors over the last few years.

In order to obtain a definite proof for the existence of shock ionization, one ordinarily measures the magnitudes of the currents for various interelectrode distances and various applied field voltages. When shock ionization is present for currents which flow across the gaps, which have widths l_1 and l_2, one may write:

$$J_1 = J_0 e^{\alpha l_1} \quad \text{and} \quad J_2 = J_0 e^{\ l_2}$$

The ratio of these currents

$$J_1/J_2 = e^{n}(l_1 - l_2) \qquad (24)$$

must be constant for electrodes of any materials.

From the curves of Fig. 70, constructed from the data of current measurements in n-hexane with l_1 = 420 microns and l_2 = 100 microns, it is clear that the relationship (24) is not fulfilled. For electrodes of copper there is almost no difference in the values of the currents (curves 1 & 2). Consequently, the increase in size of the current for the given applied field voltage is determined not so much by shock ionization as by the properties of the cathode surface, and evidently of the anode surface, as one might conjecture on the basis of the curves of Fig. 65 & 66. On the grounds of what has just been stated, the conclusions reached in reference (L. 91) should be approached carefully.

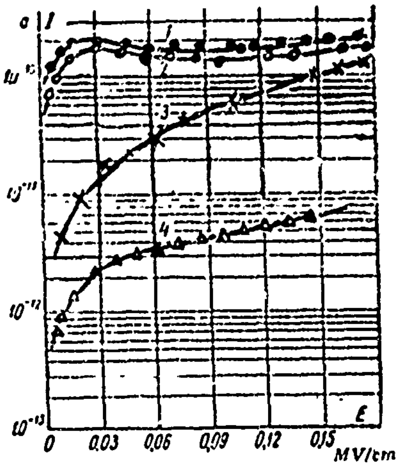


Fig. 69. I-V curves for n-hexane when the cathode material is: 1- copper; 2- nickel; 3- stainless steel; 4- gold

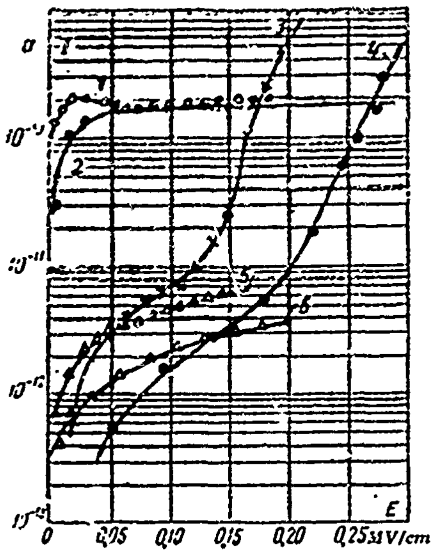


Fig. 70. I-V curves for n-hexane with cathodes: 1- of copper, 1 = 420 microns; 2- same, but 1 = 100 microns; 3- stainless steel, 1 = 420 microns; 4- same, but 1 = 100 microns; 5- gold, 1 = 420 microns; 6- same, but 1 1 = 100 microns.

The effect of the cathode surface condition on the emission characteristics in n-hexane can be illustrated with the curves of Fig. 71. It turned out that after the cathode of stainless steel is heated in air for a period of one hour at 600° C the emission rises and after heating in hydrogen at 400° C it falls (curve 3). The author of reference (L. 147) connects the growth in emission current with the formation of a comparatively highly insulating film of Fe_2O_3. Curve 3 in Fig. 71 is composed as if it consisted of two parts (see the dotted line). For E greater than 100 kv/cm the emission current rises more rapidly. In the opinion of the author (L. 147), this happens either because of an increase in the emitting area as a result of damage to the Fe_2O_3 layer, or by reason of a drop in the work-function of electrons from the cathode. The effect of the anode is not examined.

In reference (L. 43) the opposite conclusion is reached - linking the decrease in emission from the oxide cathode to a raising of the potential barrier for the discharge of electrons into liquid argon (see curve 1 of Fig. 66). But in this the assumption is made that sources for positive ions are absent and that reinforcement of the field intensity at the cathode does not take place.

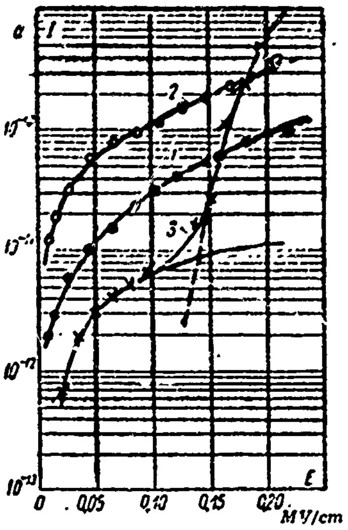


Fig. 71. I-V curves for n-hexane with a cathode of stainless steel. 1- cathode without supplementary treatment; 2- hardened at 6--° C in air for a period of one hour; 3- hardened for a period of one hour at a temperature of 400° C, but in hydrogen.

A detailed investigation of samples made from steel of the same brand, from which electrodes were fabricated in connection with reference (L. 147), showed that after thorough polishing a layer consisting of 90% Cr_2O_3 and 10% Fe_2O_3 is actually formed on the surface of the metal (L. 148).

In the preceeding paragraph a hypothesis was formed about the possible formation of a semi-conducting or insulating film on the surface of gold electrodes. According to the data of reference (L. 149), this metal at room temperature is inert with respect to O_2, N_2 and H_2, but it asorbs CO, CH_2 and C_2H_2. Therefore one might assume that the formation of some kind of film on the gold surface is indeed possible. The polished surface of copper is usually completely covered by a layer of Cu_2O running in depth from 100 to 200 Å (L. 150). This layer is semi-conducting.

Above we have presented arguments in favor of the hypothesis that the increase in current in n-hexane is determined chiefly by the emission of electrons from the cathode. But what role is played in this by n-hexane itself, or by its purification, drying and so forth? Discussion of this question also appears in reference (L. 147). Prior to the experiments the n-hexane was given a preliminary purification by various means. Separate portions of it were distilled many times. Moreover, an electrical purification was carried out over the course of a week. Other portions were kept mixed with mercury, water, concentrated H_2SO_4 and concentrated NaOH. But not one of these types of operations had even the slightest noticeable effect on the I-V characteristics of the indicated liquid.

It should be noted that these data do not completely agree with the concept about the way in which positive ions affect the intensity of electrode emission from the cathode. The number of such ions relative to the different means of purification undoubtedly underwent some variation, but the emission remained practically the same.

It might be possible to conjecture that at a given applied field voltage equilibrium was established between the approach of positive ions to the insulating layer on the cathode and their neutralization by the emitted electrons. But then the growth of emission current with an increase in applied voltage becomes not at all clear.

From what has been stated above it follows that for short pulses only some positive ions reach the cathode. A local field does not succeed in forming at its surface and the emission of electrons will be determined only by the work function and the thickness of the oxide film.

Therefore in order to form the breakdown of a liquid, the voltage must be increased relative to that voltage which has been applied over a prolonged period.

In connection with what has just been stated a question arises concerning the role of positive ions emitted from the anode. Some experimental data on this are given some consideration in reference (L. 151). The data were obtained with rectangular pulses of duration ranging from 0.25 to 54 microseconds and with the largest amplitude of 15 kv.

Breakdown was produced in pure filtered ligroin without the impurity theophene (C_4H_4S). A water solution of the electrolyte HCL, NaOH, and LiCl served as one electrode (the lower) in a vertical arranggement of electrodes. The distance between the electrodes was equal to 0.0084 cm.

It was noticed that with both pulse polarities an emission of ions took place. In regard to the effect on E_{br} of benzene their individual features turned out to be unimportant. When the concentration of ions was increased E_{br} dropped from 1.6 to 1.18 mv/cm. Such a decrease appeared somewhat unexpected for a pulse duration of 0.25 microseconds.

One should approach an evaluation of the data which we have accounted for in a very careful manner.

If the mobility of ions of the elctrolytes indicated above in ligroin do not exceed the value of 5 x 10^{-4} cm^2/v sec, found in experiments with n-hexane (L. 74), then over one second the ions may cover only about 6% of the total path-length of 0.0084 cm, and over the time of action of one pulse (0.25 microsecond) they remain practically in place.

Consequently, no field distorsion at all will occur in the gap under investigation if the mobility of these ions under high field intensities does not increase very drastically, a situation which has small probability.

In connection with what has been stated the results of experiments with so small a spark gap and with one moveable electrode should be considered not very reliable.

Chapter 5

A RELATION OF THE DIELECTRIC STRENGTH OF LIQUIDS TO CERTAIN SECONDARY PROCESSES AND SURFACE FLASHOVER

5-1. Thermal conductivity of liquids in an electric field

Some most important factors determining the process of dielectric breakdown like impact ionization, the formation of avalanches and streamers are usually referred to as primary or basis ones. Considered as secondary factors are gaseous bubbles, local overheating, the formation of three-dimensional charges etc.; they play an important role in the formation of breakdown under determined conditions and even control its development in some cases.

The curve in Fig. 35 has indicated that the breakdown voltage, U_{br}, of transformer oil for L equals 2 cm depends very much on the time of voltage switching-in. Lower values of U_{br} are observed even for times equal to tens of minutes (Table 17) i.e. for such intervals which are greater than the time of breakdown forming by several orders of magnitude.

Secondary factors certainly begin acting in a liquid when voltage close to the breakdown one is switched on, the influence of these factors increasing with time. The contribution of each above-mentioned factor can be taken for granted.

Tests have shown that a large amount of charged particles can form in the interelectrode space even without the factor of impact ionization, during the long action of voltage in a transformer oil. The presence of the particles is detected owing to the transfer of heat energy in an electric field. The particles can form three-dimensional charges near electrodes and can favor the occurrence of cold electron emission from the cathode and perhaps the impact ionization.

The tests were carried out according to the schematic shown in Fig. 72 (from 73). Thoroughly polished, brass spheres 12 cm in diameter, D, were mounted vertically in china vessel 1, 12 cm in diameter, filled with transformer oil, well-cleaned, vacuum-dried, and filtered. Heating element 2 of Nichrome was inserted in the upper sphere. The element was supplied by means of transformer 3 with 80 KV insulation. At the top of vessel 1 was located a thermometer 4, whose lower end stood at the level of the lowest point of the sphere. Another thermometer 5 was installed inside the lower grounded sphere and contacted its sufrace as shown in Fig. 72. The upper sphere was under tension of high-voltage transformer 6 either directly (alternating voltage) or through kenotrons 7 and 8 with 1-microfarad, high-voltage capacitor 9 for pulsations. Numbers 10 and 11 are assigned to the network.

At first, only the upper-sphere heating was switched on, for 2.5 hours. Temperature of the upper heated layer of transformer oil was recorded along with those of lower unheated one. The upper oil layers were heated up to a higher temperature due to convective heat transfer, while the lower ones - mainly owing to thermal conductivity. After 2.5 hours high voltage was supplied in the pulse manner to the upper sphere, and the further heat transfer between the upper and lower layers occurred in the electric field.

Fig. 73 presents corresponding curves of temperature changes in the upper and lower layers of liquid. The curves were recorded during time (2) prior to switching on 60 KV direct voltage of positive polarity (a hot cathode diode worked), and during time

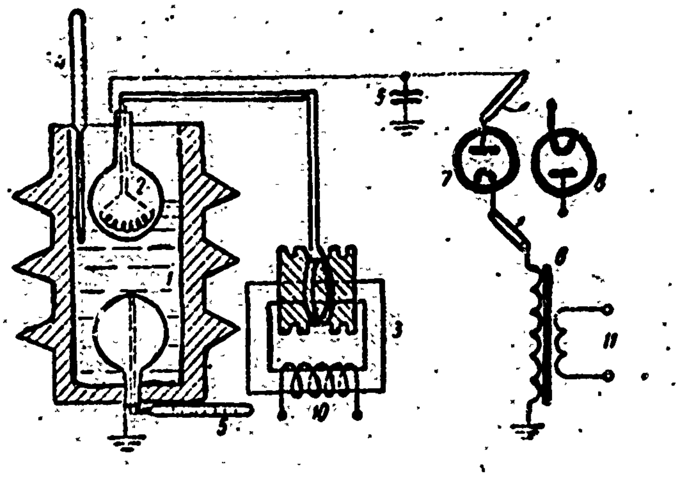


Fig. 72. Layout diagram of tests of heat transfer between layers of transformer oil heated to different temperatures.

(3) after the voltage had been connected. The distance between the spheres was equal to 6 cm (E equals 10 KV per cm).

From the curves it is evident that the temperature of upper layers of the oil rose from 20 to 110°C during 2.5 hours without voltage, and that of the lower layer changed from 20 to 26 C. The temperature increase was smooth, without any sharp jumps, which should have been anticipated. However, the lower-layer temperature was increasing very rapidly after switching the voltage on. The heat transfer occurred downwards, from above, i.e., opposite the natural course of convection.

The upper sphere was still heated after switching on the high voltage. Therefore, the temperature of upper layers again was increasing a little after the aforementioned decrease.

After the period specified in Fig. 73 the high voltage was disconnected, and capacitor 9 was discharged. Then, during period τ_3 the conditions of heat transfer between oil layers changed drastically once more. The temperature of the lower layers started to decrease, while that in the upper layers increased. After 58 minutes the same 60 KV voltage was put on the upper sphere again, and during the period of this voltage, τ_4, the heat transfer between oil layers changed sharply. Heating of the upper sphere remained unchanged. This fact also explains the increased temperature of the upper oil layers after decrease to 79°C. Judging by the curves one can conclude that the variation of the thermal conductivity of transformer oil in an electric field is very significant for heating of the upper layer to 110°C and more.

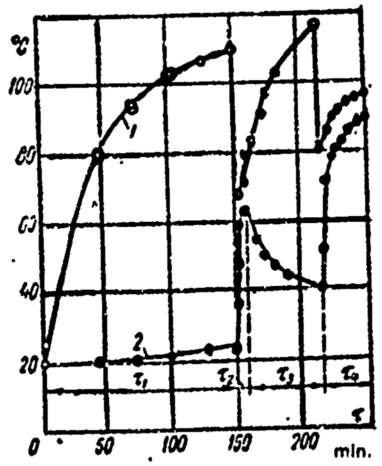


Fig. 73. Curves characterizing the heat transfer of transformer oil layers heated to various temperatures, before and after connecting a direct voltage; 1 - upper layer; 2 - lower layer.

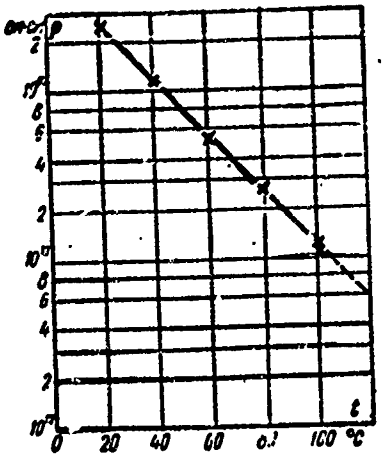


Fig. 74. Variation of volumetric resistivity of transformer oil for increasing temperature.

Variation of the volumetric resistivity of the tested oil for increasing temperatures is presented as a straight line in Fig. 74. The measurements were conducted for small voltages. The volumetric resistivity, ρ decreased to about $8\cdot10^2$ohm·cm at 110 C, which was the temperature of the upper layer of the tested liquid.

As is known, the volt-ampere characteristic of some very pure insulating liquids has the form presented in Fig. 75.

The current flowing through the section between electrodes remains constant or increases very slowly within a certain range of changes of E from 10 KV per cm and more. One can therefore assume that the amount of current carried changes also very little. As is known, the volumetric resistivity ρ can be determined in terms of this amount of ions, n, their charge, e, and mobility, k_0, as follows:

$$\rho = \frac{1}{nek_0} \text{ and } n = \frac{1}{\rho e k_0}. \quad (25)$$

Referring to the mobility of negative ions in transformer oil, it is known that it equals about 0.0001 sq cm per sec · V [52] near room temperature. According to bibliographical sources, the mobilities of negative and positive ions do not differ very much (3) for some other insulating liquids. Therefore the mobility of positive and negative ions of transformer oil can be assumed to be the same, in rough calculations.

As was reported, the mobility k_0 and viscosity η of liquid dielectrics are interrelated through formula (16). For the temperature of transformer oil changing from 20 to 110 C, the viscosity of the oil decreased by about 33 times. Therefore, the value of k_0 at t equal to 110 C will be 200 times greater, i.e. 0.0001·200 or 0.02 sq. cm. per sec. · V, with $n=4\cdot10^{7}cm^{-3}$. This amount n is about $1.6\cdot10^{10}$ ions throughout the whole volume (400 cub cm) of the heated layer. Half of this amount will transfer an energy of

$$\frac{n}{2}\cdot\frac{mv^2}{2} = \frac{3nkT}{4} \approx 1{,}5\cdot10^{-11} \text{ cal.} \quad (26)$$

during its motion towards cooler, lower layers of transformer oil. After the passage of these ions to the lower layer of the vessel, their place is taken up by molecules with smaller kinetic energy from lower layers. Dissociating into ions during heating these molecules also drop downwards; some $1.4 \cdot 10^{15}$ ions that transfer the energy of about $1.3 \cdot 10^{-6}$ calories can pass to the lower layers in one hour. The transferred amount of energy remains small also in the case when a possible increase of the mobility of ions due to the decay of heavy particles into lighter ones is taken into account. Only a portion of this energy can be given to molecules with smaller kinetic energy. An approximate calculation according to the formula by Frenkel (53) has shown that the ratio of the oil conductivity for E equal to about 10 KV per cm to the conductivity for very small E is about 2.

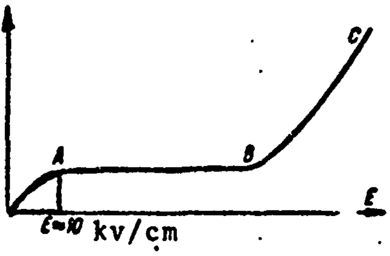


Fig. 75. Volt-ampere characteristic of pure insulating liquids.

It is well known that the conductivity is usually measured for several minutes after voltage has been disconnected. The conductivity decreases as a continuous function to a steady value during that time. It will be mentioned in § 6-1 that the original conductivity, e.g. in n-hexane can differ from the steady value by as much as two orders of magnitude. But even considering this fact, the energy transferred by ions with normal conductivity would not have been enough to heat up 900 grams of transformer oil for a heat content equal to about 0.5 cal per G · °C. Accordingly, such an intensive heat transfer had not occurred by means of normal-conductivity ions.

It can be assumed that dissociation of a very great amount of ionic groups of liquid molecules was taking place at 110 C in such a way that the dissociated groups remained connected through the Coulomb interaction forces and they behaved like neutral complexes for small voltages. The final breakdown of these bonds occurred for voltages of several kV per cm.

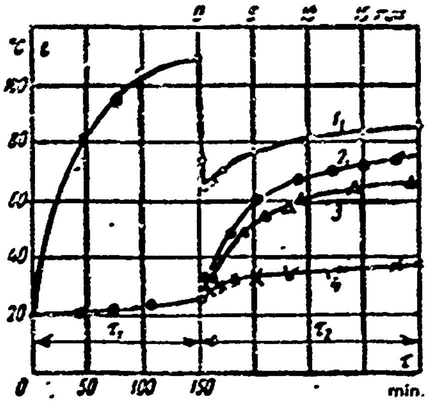


Fig. 76. Curves of heat transfer between layers of transformer oil heated up to different temperatures. Curves 2,3, and 4 are drawn according to readings on thermometer 5 in Fig.72. 1 and 2 - E equal to 10 KV per cm; 3 - E equal to 5 KV per cm; 4 - E equal to 2.5 KV per cm.

If such an "incomplete" dissociation existed in reality, the heat transfer between the layers would be less intensive for smaller voltages applied. Tests conducted for 10; 5, and 2.5 KV per cm have confirmed this finding (Fig. 76).

The transformer oil was heated under identical conditions before applying the voltage (for time τ_1), and thus the process is represented only by one curve (1). The variation of the temperature of the upper liquid layer after connecting various E is also described by only one curve, recorded for E equal to 10 KV per cm. The upper sphere was heated without interruption. Curves 2 to 4, characterizing the temperature variation of the lower layers of liquid, have been recorded for field voltages equal to 10; 5, and 2.5 KV per cm, respectively.

Furthermore, the tests have revealed that no significant heat transfer between liquid layers is observed in practice for E equal to 10 KV per cm of alternating voltage (50 Hz; amplitude value). It has also been found that, during turbulent heat exchange, heating of transformer oil by conductive currents does not play any role of importance. Basically, this kind of heat transfer has also been revealed in pentachlorodiphenyl.

Can the failures of electrostatic bonds of ionic complexes occur at lower temperatures, e.g. close to room temperature? It has been reported above that even well-degassed transformer oil is observed to give off hydrogen if direct voltage is applied. According to bibliographical sources [67] this takes place for E equal to about 40 KV per cm near room temperature, or for E equal to 12 to 16 KV per cm, after [68]. The specified discrepancy is apparently due to chemical properties of crude oils from which the tested oils were produced.

The emanation of hydrogen can be assumed to occur just for breakdowns of weakly-bonded ion complexes. But the same seems to be possible in the case of the chemical interaction of molecules of saturated and unsaturated hydrocarbons according to the scheme [154]:

$$C_nH_{2n} + C_mH_{2m+2} \rightarrow C_{n+m}H_{2(n+m)} + H_2.$$

By definition, an electric field somehow stimulates that interaction.

If direct voltage is applied for a long time, space charges, bringing about a redistribution of the field potential within the interelectrode section, can form as a result of the motion of ions of the broken complexes. The progressive formation of breakdown can begin at a lower E. This will be promoted by hydrogen emanation during breakdowns, too. Gas bubbles in insulating liquids usually reduce the breakdown voltage. One can assume that the greater the distance between electrodes, the more significant is the influence of those space charges.

Some authors believe that the electrical conductivity of well purified and non-polar liquid dielectrics for voltages up to 1 KV per cm is affected by the ionization of cosmic rays and the Earth's radiation [155, 156]. In the case of greater field intensity, an additional component is involved due to the emission of electrons from the cathode, and due to the impact ionization [157, 158].

According to the foregoing, it is charged particles, formed as a result of breakdowns due to the field of weakly-bonded ionic aggregates that are also added to the above sources in transformer oil and pentachlorodiphenyl.

Turbulent heat transfer in an electric field between regions of transformer oil heated to different temperatures, can be of practical interest, for instance, in designing high-voltage oil-filled, direct voltage equipment.

5-2. Changes in the structure and properties of liquids under the influence of irradiation

The influence of irradiation should be taken into account in the operation of oil-filled electrical equipment of nuclear power plants and mobile power stations using nuclear energy. The electrical insulation properties of liquids can change many things in the field of intensive irradiation. In general, irradiation does not necessarily impair these properties. In many cases, irradiation can bring about their amelioration due to changes in the chemical composition of a dielectric. Also, new electrical insulation materials can be synthesized using irradiation.

The influence of irradiation should be taken into account in the operation of oil-filled electrical equipment of nuclear power plants and mobile power stations using nuclear energy. The electrical insulation properties of liquids can change many things in the field of intensive irradiation. In general, irradiation does not necessarily impair these properties. In many cases, irradiation can bring about their amelioration due to changes in the chemical composition of a dielectric. Also, new electrical insulation materials can be synthesized using irradiation.

Intensive and prolonged irradiation is apt to bring about a transition from the liquid state to gels or the solid state and also to stimulate progressive oxidation of a substance. Simultaneously, its viscosity can increase and its electrophysical properties can get worse.

It has been found that the formation of transverse bands and splitting of molecular chains brings about the breakdown of many polymers [159, 160]. A material will be resistant against irradiation only if it is apt to absorb the radiation energy without extraordinary ionization and if double bands form in it without breakdown of chains during this absorption.

Tests and practice have shown that fluoridated materials have a weak radiation resistance. A liberated fluorine atom breaks the carbon-carbon band. Under these conditions a non-combustible and explosion-resistant electrical-insulating liquid-hyperfluoroxylester, which does not break down even at 300 °C can be unstable.

Among polymers with phenyl groups, the most stable are those with the benzene ring located at the side instead in the main chain. Very extensive information has been obtained on the radiation resistance of polymers [161]. The relationship of the structure of these compounds and the radiation resistance is illustrated in Fig. 77. It shows the recurrent links of the chain structure distributed in accordance with decreasing stability [160 and 162]. Individual regularities in changes of these solid substances can apparently be extended to liquids, too.

Irradiation by ALPHA- and BETA-particles, due to their low penetration ability, is usually absorbed by the upper layers of a substance. The change of structure and decreased conductance were observed [163] in synthetic ceresine under BETA-irradiation from a source of radioactive phosphorus P^{32}. Ultraviolet radiation originates in the ionization of liquids and increases their conductance. Tests of this kind were conducted with solutions in ethyl esters of chlorobenzene, bromobenzene, and iodo-oxybenzene. The conductance decreases sharply [164] after irradiation has stopped In contrast to ALPHA and BETA rays (corpuscles), GAMMA-photons have a very high penetrability and interest with orbital electrons of the substance immediately within the whole bulk.

During collisions with those electrons, GAMMA photons push them out of primary orbits. A displaced electron can receive an energy of several mega-electronvolt (MEV). The ionization potential and excitation potential of molecules of insulating liquids usually do not exceed 15 kV. Therefore such an electron is able to ionize and excite several thousand molecules or more. The same can be done by an electron of BETA radiation with the specified energy. Thus, ionized and excited molecules are originated in organic matter in the field of intensive radiation, some chemical transformation being apt to occur within this medium.

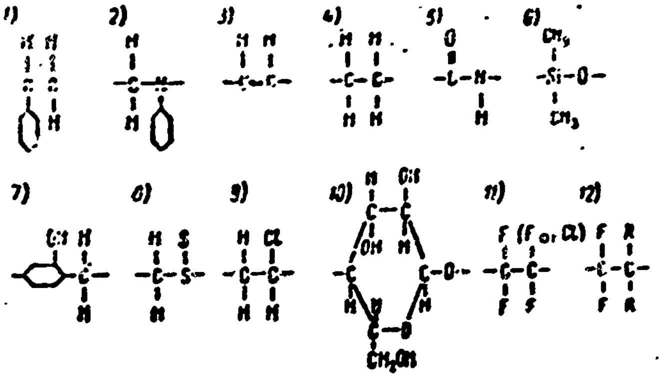


Fig. 77. Chemical formulas of substances arranged according to decreasing irradiation resistance, from 1 to 12. 1 - polystyrene link; 2 - polyanilineformaldehyde link; 3 - a link characteristic of the structure of most elastomers; 4 - polyethylene link; 5 - nylon link; 6 - silicon-organic rubber link; 7 - phenol-formaldehyde resin link; 8 - thiocol link; 9 - polyvinyl chloride link; 10 - cellulose link; 11 - a link in the structure of polytetrafluoroethylene and polytrifluorochloroethylene; 12 - the link of polymethylmetacrylate, butyl rubber, and polyalphamethylstyrene.

Ionization of molecule M under collision of a GAMMA-photon with an orbital electron e follows the equation

$$M + \gamma \rightarrow M^{+} + e.$$

An ionized molecule under recombination with electron e can form an excited molecule

$$M^{+} + e \rightarrow M^{*}.$$

Excited and ionized molecules can disintegrate spontaneously with the liberation of hydrogen and the formation of radicals R or other molecules having a lower molecular weight

$$M^{+} + e \rightarrow R + H.$$

Moreover, molecules with linear chains are able to rearrange themselves and form branched chains. Free atoms and radicals, in turn, can promote the formation of new compounds - mostly unsaturated.

Aside from hydrogen, complexes of carbon dioxide or other small groups can split away from a long and complex molecule while absorbing the energy of GAMMA-quanta.

It has been shown that, for example, during the irradiation of transformer oil with a dose of 1,000,000,000 Roentgens liberation of gas occurs, the volume of which is 10 to 15 times that of the oil itself. Such a reaction in a closed vessel can bring about a considerable pressure increase.

Molecules being split can shorten up to one-half or one-third of their initial length. The viscosity of a substance diminishes. If transverse bonds of the links of molecular chains form during the absorption of the energy of GAMMA-quanta, the process of polymerization is likely to happen, and a liquid substance can be converted into a solid. The higher the specific weight of a liquid, the more intensive is the interaction of GAMMA-photons and electrons of molecules.

The influence of irradiation on the electric properties of certain liquid dielectrics was studied by means of a cobalt radioactive source (Co^{60}) with an intensity of 2300 Curies. A preparation in several air-tight cylinders of stainless steel was immersed in water layer 3.6 m deep.

The tested liquids were poured into sealed glass vials and were immersed in the field of (Co^{60}) radiation. Some physico-chemical properties of the tested liquids are presented in Table 31. As is known, transformer oil consists mainly of a mixture of isomeric hydrocarbons of the paraffin series $CH_3\ (CH_2)_{20}CH_3$ and naphtenes.

Table 31

Some physico-chemical properties of the tested liquids

Liquids	Average molecular weight	Pour Point °C	Flash point °C	Acidity milligrams KOH
Transformer oil	330	-40	135	<0,01
Castor oil	975	-13	515	0,12
Trichlorobenzene	181	17	195	0,01
Pentachlorodiphenyl	326	10	-	<0,01
Silicone liquid	300	-84	315	<0,01

The structural formula of naphtene hydrocarbons is presented in Fig. 78,1. The oils also include traces of unsaturated compounds and oxidation products of hydrocarbons - quinones (see Fig. 78,2). The chemical composition of oils depends on the oil field and the degree of distillation.

Castor oils are produced by pressing seeds of the castor oil plant. Basically, it consists of the glycerin of ration acid (see Fig. 78,3). The oil comprises three hydroxylic groups able to form hydrogen bonds.

Trichlorobenzene (Fib. 78,4) has three isomers. 1,2,4-trichlorobenzene was subject to irradiation. It was mixed with pentachlorodiphenyl (chlorinated biphenyl, sovol) to avoid its

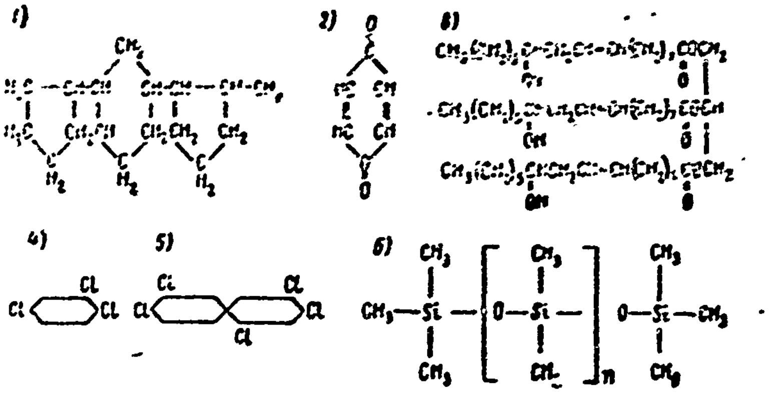


Fig. 78. Structural formulas of liquid dielectrics
1 - naphtene hydrocarbons; 2 - quinones; 3 - castor oil; 4 - trichlorobenzene; 5 - pentachlorodiphenyl; 6 - silicone liquid.

solidifying at 17°C [165,166]. This insulating liquid was obtained as a result of the interaction of chlorine and diphenyl (see Fig. 78,5). Dielectric losses of sovol are reported in [167]. Abroad, materials of that kind are called piranol, inertin, clophene, permitol, and arochlor. The latter is almost an electric-insulating liquid IN-420 with E-BR equal to 0.2 MV per cm [168]. 0.25 to 0.5 percent of antraquinone is added to stabilize such liquids in some cases [169 and 170].

As was reported, silicone liquid (silicone oil) is produced by hydrolysis and next condensation of dimethylchlorsilane or its analogs (see Fig. 78,6).

The liquids were irradiated for the time ranging from 5 hours to 1 month. This has corresponded to the dose of 2.5 to 84.1 Mega Roentgen (equivalent physical). One physical equivalent Roentgen (F.E.R.) is the dose of any irradiation, for which the energy absorbed by 1 G of a matter is equal to the energy lost for ionization occurring in 1 G of air due to 1 Roentgen coming from a source of X-rays or Gamma-rays. The dose of 1 F.E.R. corresponds to the formation of about 2.8 x 10^9 ion pairs per 0.001293 grams of air.

The most significant structural changes have been observed in silicone liquid. For the dose of 30 M F.E.R. this liquid transformed into a rubber-like gel substance, then into a brittle, transparent one, and finally - into a powder. Such transformations have confirmed the process of polymerization, the formation of cross-structures (gel-formation) and the breakdown of chains (the formation of powder). The greatest impairment of electric properties has been observed for transformer oil.

Trichlorobenzene and pentachlorodiphenyl change color under the influence of irradiation. They become turbid due to the great amount of gases emanated inside.

Data on changes of ϵ and tgδ of liquids after irradiation is presented in Table 32. The measurements were conducted at 1 KH_z frequency. The table shows that the dielectric penetrability of transformer oil increased by a factor of about 4, and that losses increased very much too. After irradiation the oil transforms into a polar liquid. Increase of tgδ is apparently due to greater conductance, since it is observed along with a considerable decrease in volumetric resistivity. The pH of the oil increases. Castor oil has proved to be most resistant. Its changes of ϵ and tgδ are insignificant. The authors infer that this is a consequence of the unsaturated nature of the radical acid.

On converting the pH numbers for 1 cubic cm of a tested liquid and on absorbing 100 EV energy it has been shown that the

Values of ε and tgδ of liquids before and after GAMMA-ray radiation

Liquids	Radiation dose M FER	Values of ε		Radiation dose M FER	Values of tgδ%	
		before radiation	after radiation		before radiation	after radiation
Transformer oil	43	2,23	8,59	43	0,30	75,00
Castor oil	43	4,46	4,59	43	0,50	0,80
Trichlorobenzene	4	4,11	4,15	47	11,4	44.21
Pentachlorodiphenyl	7	5,04	5,10	7	0,5	2,71
Silicone liquid	24	2,73	2,77	24	0,3	1,21

calculated acid equivalent is greatest for pentachlorodiphenyl, and smallest for silicone liquid. Hydrochloric acid is given off during the decomposition of pentachlorodiphenyl, while hydrogen is liberated from silicone acid.

It was mentioned above that ionized and excited molecules, along with free atoms and radicals, can form during absorption of GAMMA radiation in liquids. It has been shown that the rate of destructive processes in liquid can be inhibited by introducing substances able to react with product of decomposition and to form unreactive stable complexes. Such properties are, for example, characteristic of derivatives of quinone and diphenylpicrylhydrosil.

Isooctane (C_8H_{18}) and liquid hydrogen, for instance, have shown their conductance to increase more slowly with increasing field strength after irradiation, as compared to before irradiation [127]. The authors of the cited work argue that a compact column of ions forms in the direction of GAMMA-rays in liquids, with intense recombination taking place inside. A considerable field strength is required to split out charges in the column.

If charged particles rebound quickly, it is not suprising that, in many cases, GAMMA-radiation does not play any important role with respect to E_{br} of liquids. This has been proved, for instance, in tests with n-hexane irradiation with radioactive cobalt [86 and 90].

The same result was obtained on exposing the above mentioned liquid to the action of a radium source. The tests in this case were conducted with rectangular pulses of 3 microseconds [91]. The action of this radiation brought about only a certain decrease in the delay time of the formation of breakdown. In the case of direct voltage, a certain decrease of E_{br} has been revealed in transformer oil during its irradiation by radioactive cobalt [127]. The spark gap was equal to 0.5 millimeter. Any decrease of E_{br} was not observed for short pulses.

According to the data of [171], significant pulsations of current arise in liquid argon under the action of GAMMA-irradiation and field strength E, equal to 10 KV per cm. It was assumed that they are caused by electron avalanches. The intensity of pulsation decreased after oxygen and nitrogen had been introduced to liquid argon. However, they are always present in n-hexane. Oxygen and nitrogen molecules apparently capture free electrons created during irradiation.

The pulsations are not observed in liquid nitrogen or n-pentane in irradiation by ALPHA-corpuscles from a polonium source [172,173]. According to the opinion of the authors of the works cited above, the free-path length of electrons in n-hexane and n-pentane is very small and they are quickly captured by molecules of the liquids indicated.

Processes of self-oxication are stimulated in hydrocarbon compounds under the action of GAMMA radiation. In this regard, irradiation acts as a catalyst. During the systematic investigation of the action of GAMMA-quanta on the process of self-oxidation of organic compounds, including hydrocarbons, it was revealed that all oxidation products, i.e. aldehydes, alcohols, acids etc. are originated during decomposition of basic molecules [174]. It is thus quite obvious that E_{br} will decrease, for instance, with an increase in the pH of the transformer oil. A certain decrease of E_{br} in a given liquid is likely to occur as a result of this phenomenon in the case of direct voltage. It is impossible to detect the decrease of E_{br} in the case of short pulses.

It seems correct to assume that the rate of aging under the action of GAMMA-irradiation is affected by the chemical composition of hydrogen compounds and their structure. The process of aging will be more intense in certain liquids than in others, but in most cases one should expect an impairment of electrical properties due to increased acidity, even if only after a long time.

By the example of paraffin oxidation it has been proved that the induction period, i.e. the time without any perceptible self-oxidation, is reduced from 370 to 12 hours [175] under the action of irradiation from a source of 4.3 curies located 30 cm away. This is also confirmed by tests with n-hexadecane [176].

5-3. Aging processes in liquids

Irreversible changes of mineral oils occur in use, primarily due to oxidation. Acids, resinous substances, and deposits are formed along with volatile and unvolatile oxygen compounds during the interaction of oxygen and hydrocarbon molecules of oils [177]. Acids destroy the cotton insulation of transformer windings and certain insulating parts. Increased acidity impairs the dielectric properties of oils themselves. The breakdown strength does not diminish. As a result of deposits on the insulation of windings, the heat transfer from wires to oil decreases due to smaller thermal conductivity. A normal thermal regime can be broken down, and a facility can be set out of order.

The amount of oxygen soluble in a mineral oil depends on temperature, outside pressure, as well as the fractional and chemical composition of the oil. The degree of oil refinement is of great importance, too. It is known [178] that naphtene-paraffin oils absorb oxygen most readily. Aromatic hydrocarbons absorb it to a lesser extent, and oil distillates even less.

Tests have shown that the process of oxidation begins at the surface gradually penetrating the body of oil. The reaction of oxidation is stimulated by solar light and, as was mentioned in the previous section, by GAMMA-radiation. The absorption of oxygen by oil under light is quite intensive even at normal temperatures. The violet and ultraviolet spectrum ranges are active with regard to transformer oil.

Oxidation occurs more intensively if the oil is clean [179]. It is well-known that oxidation of hydrocarbons by molecular oxygen is accelerated very much in the presence of certain metals and their organic salts. For instance, almost complete oxidation of paraffin can be achieved at 150 C in 5 hours in the presence of manganese oxides. Vanadium, too, strongly accelerates oxidation [180]. Such compounds are called positive catalysts.

According to certain data, the formation of deposits accelerated in an electric field. Acids formed in oil are assumed to transform into deposits under the action of the field [181]. In other opinions, an electric field promotes coagulation of deposits in a fine dispersion [182]. However, there is no general agreement as to this point. For example, the influence of an electric field on the formation of deposits is negated in the work [183]. The deposition and the increase of pH-number in oil during the exploitation of transformers depends on the sort of crude oil (see Table 33), and the degree and character of purification of oil itself.

Table 33

Oxidation of transformer oils obtained from various crude oils

Oil field	Duration of oil use months	Acidity in milligrams of KOH	Asphaltene and acid content %
Embinskoye (dossor-makatskoye)	4	0,306	-
	10	0,889	net
Bibi-eybatskoye (light oil)	4	0,397	0,108
	10	1,700	0,480
Bakhalanskoye (heavy oil)	4	0,560	-
	10	1,860	0,101

Aromatic hydrocarbons, e.g. benzene, without side chains in the molecular structure oxidize little in air. Some chemical transformations can be observed in benzene or its closest homologs only in the presence of catalysts or ozone, at higher temperatures, or under higher pressures. Aromatic hydrocarbons are more susceptible to oxidation The more rings the more complex the structure [184]; the same is observed for increasing lateral chains and their lengths.

It is well known that, along with substances promoting oxidation, there exist compounds inhibiting the reaction of self-oxidation. These compounds are called anti-oxidants or inhibitors. The inhibitors are widely used in practical applications.

The following requirements should be satisfied by inhibitors:

1. their fair solubility in oils without entering into reaction with them and and no precipitation at lower temperatures;
2. no impairment of the dielectric properties of transformer oils or the demulsification capacity of turbine oils;
3. no solubility in water (or very little) and no decomposition under the influence of water or metals;
4. no promotion of the corrosion of metals, especially iron and copper;
5. no chemical changes under long dissolution in oil;
6. no evaporation at operation temperatures in oil-filled equipment and no hygroscopic properties.

In the work [185] it was found that the oxidation of readily oxidizing substances can be inhibited with the following chemical compounds: hydroquinone, pyrogallol, naphthene, tannin, organic bases, iodine alkyls, carbon tetrachloride, sulfur, sufuric compounds, phosphorus, inorganic and organic sulfides, amines, carbonamides, uretanes, various dyeing agents, inorganic halogens, inorganic compounds of phosphorus, arsenic, antimony, bismuth, sodium banete, silicon, lead, tin, and a number of others.

The mechanism of the action of inhibitors (negative catalysts) is explained in terms of chain reactions [184 and 186], in which the energy of a reaction does not transfer into heat energy, but rather passes completely to adjacent molecules and activates them before the next reaction. Receiving this energy, inhibitors do not supply it to other molecules but dissipate it and break chains; the reaction is broken down.

According to the data of [187], sulfur is a good antioxidant of transformer oil. Adding it at 0.15 percent at 130 to 140 C diminishes the formation of deposits by a factor of about 6 in the course of 130 to 168 hours. Compounds like phenylhydrazine, cymene, turpentine, iodoform, pseudocumene, menthol, furfural, etc. decrease the formation of sediments by half or more. On the other hand, phenyltheomethane increases this formation by the factor of 6.6, and n-phenylenediamine increases it by a factor of 12.4. After [188], high antioxidizing properties are characteristic of hydroquinone, pyrogallal, oxyhydroquinone, tin naphthenate, and monosulfides containing at least one oliphatic group at sulphur atom (cetylphenylsulphide) [189]. Among acids, maleic and citraconic ones have these properties.

The time required to develop the reaction, when perceptible oxidation does not occur, is called the induction period, as was mentioned in the preceding section. In the work [190] they showed that only the induction period is extended in mineral oil when antioxidants have been introduced (Fig. 79). The ordinate axis in Fig. 79 shows the acid content in oil (percent), while the abscissa axis denotes the oxidation time in hours. The parallel layout of the curves confirms that once initiated, the reaction of self-oxidation always develops with the same rate, independently of whether pure oil is under oxidation or an inhibitor has been added.

Some additives increase the induction period by several times [191]:

Oxidized mixtures	Induction period of oxidation hours
Original oil	72
Same oil plus 2.4-dimethyl-6-fluoro-butylphenyl	150
Same oil plus 2.6-di-tert-butyl-4-methylphenol	575

According to the data of [187], sulfur is a good antioxidant of transformer oil. Adding it at 0.15 percent at 130 to 140 C diminishes the formation of deposits by a factor of about 6 in the course of 130 to 168 hours. Compounds like phenylhydrazine, cymene, turpentine, iodoform, pseudocumene, menthol, furfural, etc. decrease the formation of sediments by half or more. On the other hand, phenyltheomethane increases this formation by the factor of 6.6, and n-phenylenediamine increases it by a factor of 12.4. After [188], high antioxidizing properties are characteristic of hydroquinone, pyrogallal, oxyhydroquinone, tin naphthenate, and monosulfides containing at least one oliphatic group at sulphur atom (cetylphenylsulphide) [189]. Among acids maleic and citraconic ones have these properties.

The time required to develop the reaction, when perceptible oxidation does not occur, is called the induction period, as was mentioned in the preceding section. In the work [190] they showed that only the induction period is extended in mineral oil when antioxidants have been introduced (Fig. 79). The ordinate axis in Fig. 79 shows the acid content in oil (percent), while the abscissa axis denotes the oxidation time in hours. The parallel layout of the curves confirms that once initiated, the reaction of self-oxidation always develops with the same rate, independently of whether pure oil is under oxidation or an inhibitor has been added.

Some additives increase the induction period by several times [191]:

Oxidized mixtures	Induction period of oxidation hours
Original oil	72
Same oil plus 2.4-dimethyl-6-fluoro-butylphenyl	150
Same oil plus 2.6-di-tert-butyl-4-methylphenol	575

However, not only a lengthening of the induction period, but also a considerable decrease of the intensity of subsequent self-oxidation has been revealed [177] for some other liquids with pyrogallal introduced.

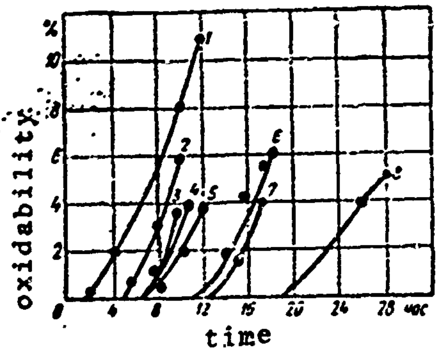


Fig. 79 . Oxidability of oils as a function of time; inhibitors at 130 C. 1 - pure oil; 2 - the same plus 0.01-percent BETA-naphthylamine; 3 - the same plus 0.01-percent naphthylamine; 4 - the same plus 0.01-percent n-aminophenol; 5 - the same plus 0.01-percent diphenylamine; 6 - the same plus 0.05-percent diphenylamine; 7 - the same plus 0.01-percent phenyl-BETA-naphthylamine; 8 - the same plus 0.01-percent diphenylhydrazine.

It was noticed that thoroughly-cleaned oils, homogeneous in their composition, are easier to prevent from oxidation, as compared against poorly cleaned ones [177 and 192]. Some stabilization due to the addition of 0.01 to 0.1-percent para-oxydiphenylamine takes place only in transformer oils supplementarily cleaned with sulphyric acid. Effective sulfanilylamide compounds reduce the accumulation of oxide products in oils by a factor of 7 and precipitates by four to six times.

It should be mentioned that adding some antioxidants (n-oxydiphenylamine, phenyl-BETA-naphthylamine, etc.) must be conducted up to the beginning of the active process of self-oxidation. However, other antioxidants (ALPHA-naphtol, ALPHA-naphtylamine, etc.) are effective only if introduced after the beginning of the process. A third group of additives inhibits the process of oxidation when added before the beginning of self-oxidation, but stops this reaction only if the process of oxidation has not developed too far (this group includes BETA-naphtyl, 2.6-di-tert-butyl-4-methylphenol). The action of these oxidants does not depend on their concentration in oil [193].

Tests [192 and 194] have shown that introducing certain anti-oxidants into transformer oil not only does not impair its dielectric properties but even improves them (see Tables 34 and 35). Breakdown voltage in Table 34 is shown for the standard gap equal to 2.5 mm.

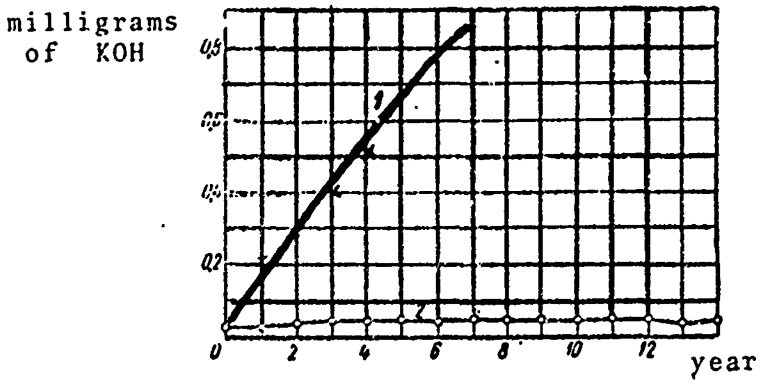


Fig. 80. The acidity of turbine oil as a function of time. 1 - oil without antioxidant; 2 - oil with antioxidant.

Fig. 80 shows curves that illustrate the stabilizing action of turbine oil in turbine generators [195]. Acidity in milligrams of KOH per 1 gram of oil is represented on the axis of ordinates, and the abscissa axis denotes operation time in years. Acidity of the oil without antioxidants increased to 0.8 milligrams of KOH during 6 years of operation, and the oil was replaced. The stabilized oil, however, has been under operation for 14 years and its acidity has not exceeded 0.1 milligram of KOH.

The stabilization effect of transformer oil in high-voltage terminals of oil switches is illustrated by curves in Fig. 81.

Table 34

Breakdown voltage of transformer oil with various antioxidants

Transformer oil	Amount of additives	Breakdown voltage,KV
"Triple mixture" without additives.......	-	35.6
The same plus phenyl-BETA-naphtylamine...	0.01	44.8
" " " p-oxydiphenylamine.........	0.01	46.4
" " " "	0.10	47.4
Nebitdagskoye transformer oil without additives........	-	42.8
The above plus p-oxydiphenylamine........	0.01	42.8

[after 192]. The ordinate axis represents acidity in milligrams of KOH for 1 gram of oil. With antioxidant VTI-1 added, the oil has worked for 10 years without significant increase of acidity. The oil without additives increased his acidity sharply under the same conditions.

Table 35

Dielectric losses of transformer oils for E equal to 10 KV per cm

Transformer oil	Temperature of oil, °C	tgδ, %	
		without antioxidant	with antioxidant
Fresh I	40	0.1	0.2
	60	0.5	0.5
	80	1.8	1.5
Fresh II	20	1.7	0.9
	40	2.6	1.7
	60	3.8	2.2

There are hints [196] as to the expediency of introducing additives into an adsorbent (silica-gel, active aluminum oxide), which would pass oil during operation. This procedure has been shown to stabilize oil better than additives introduced directly into oil. By applying an adsorbent and antioxidizing additive they managed to increase the operation period of transformer oil by a factor exceeding 15.

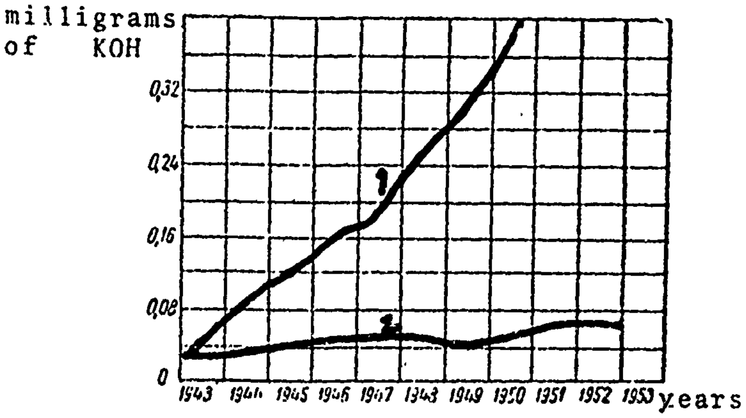


Fig. 81. Changes in acidity of transformer oil in oil-filled terminals of 110 KV switches
1 - oil without additives, 2 - oil with antioxident VTI-1

However, cases are known when adding antioxidants did not cause such a significant effect. According to the data of [197], the following is required to bring about the effect of stabilization:

1. oil to stabilize should be completely free of impurities (mechanical additions, slurry, etc.);

2. oil-storing reservoirs should be extremely clean and air-tight;

3. pumping equipment and oil ducts should also be clean.

Aging of mineral oils takes place during ionization processes, as well. A solid high-molecular compound (wax) of light-yellow or dark-brown color is formed during that time. The compound is non-combustible and unvulnerable to common organic solvents.

The formation of wax during ionization is usually accompanied by the liberation of hydrogen and volatile hydrocarbons having low molecular weight. This process is also possible without emanation of gases during the polymerization of unsaturated hydrocarbons.

The wax is produced in relatively large amounts during the generation of paper-oil power cables. This can be easily exposed after dissolving impregnating agents and dyeing paper bands with for example, red dye. The wax remains undyed. Its occurrence is usually deemed to be the initial stage of the aging of cable insulation.

Some data has been furnished above as to the possible influence of an electric field on the formation of deposits in transformer oil. On the basis of the foregoing, one can assume that wax is the form of fine-particle sediment is also formed in ionization processes in gas bubbles in transformer oil.

Large amounts of soot are created during dielectric discharges in non-flammable and explosion-proof pentachlorodiphenyl (sovol) and sovtols. Therefore, field strengths for these insulating liquids should not exceed corona voltages. Only emanation of gases is observed in transformer oil under analogous conditions.

Sovtol-2 is a Russian name of the mixture containing 64 percent of chlorinated biphenyl and 36 percent of trichlorobenzene. Sovol and sovtol in dielectric arcing emanate a large amount of hydrogen chloride (about 98 percent), some gaseous (unsaturated) hydrocarbons (about 0.16 percent) and very little carbon monoxide (traces). Neither carbon dioxide, chlorine, or phosgene ($COCl_2$) occur under the specified conditions [166].

The process of aging is particularly pronounced in paper capacitors impregnated with pentachlorodiphenyl in direct voltage. Increasing current leakage is observed after a certain time of operation. Corrosion occurs on aluminum foil, and especially on the positive lining, and the paper of sections becomes covered with brown patches.

Corrosion of that kind is considered to be due to the action of hydrochloric acid, traces of which are always present in pentachlorodiphenyl. During decomposition, its chlorine ions move in the electric field towards the positive lining and form $AlCl_3$ while interacting with aluminum. The compound promotes decomposition of pentachlorodiphenyl and the formation of new portions of HCl, which destroy paper insulation.

In order to reduce the intensity of aging, inhibitors are being introduced in pentachlorobiphenyl; they capture Cl^- or H^+ and hinder the formation of HCl. One of such inhibitors, mentioned in section 5-2, is antraquinone $[C_5H_4(C - 0)_2C_5H_4]$. The use of octadecylene $(C_{18}H_{36})$ has also been reported.

Acidity of sovtols after heating at 110 C during 30 days does not increase more than twice in the presence of materials such as transformer steel, winding copper, hetinax, cable paper and rubber. The amount of the specified materials was taken in the tests 1.5 or 2 times greater than in common oil-filled transformers. The breakdown voltage of sovtols did not change only when transformer steel coated with "202" enamel was used during heating. It increased from 42.8 to 57.3 KV (for 2.5-mm standard gap) during heating with other materials.

The dielectric losses of sovtol, measured for 1 KV and 50 Hz in the presence of various materials change during heating in the following way:

	tgδ at 20°C	tgδ at 90°C
Original sovtol (before heating)........	7×10^{-4}	1.24×10^{-2}
After heating at 30°C during 30 days....	7×10^{-4}	1×10^{-2}
After heating with transformer steel coated with 202 enamel..............	1.1×10^{-3}	9.7×10^{-2}
The same, but with winding copper PBO...	-	7.44×10^{-2}
The same, but with hetinax pipes-.......	6×10^{-4}	8.53×10^{-2}
The same, but with cable paper..........	1.7×10^{-3}	5.9×10^{-2}
The same, but with rubber...............	0.15	>1.0

From the presented data one can see that the dielectric losses increased greatly only when heating sovtols with rubber. It is worth noting that U_{br} of liquids also increased to 52 kV.

High stability of oils of the octol type was noticed during their use as impregnating agents for high-tension cables. In an electric field, octol does not give off hydrogen, as mineral oils do, but absorbs it. A mixture of oil and colophony has the same property. From the viewpoint of dielectric strength, this circumstance is important for inhibiting the formation of gas bubbles.

Solid products of polymerization such as wax are not formed in the long operation of paper capacitors impregnated with octol-type oils.

Volumetric resistivity decreases little in certain sorts of fluororganic compounds subjected to thermal aging. Under the action of an electric arc they are decomposed with an emanation of carbon monoxide and carbon dioxide, and saturated as well as unsaturated fluoride compounds. The latter are corrosive to metals and insulating materials.

Some decomposition products are toxic. Any significant influence of fluororganic liquids on metals and solid dielectrics under long and joint heating has not been revealed.

It has been reported in section 2-4 that lectronol absorbs more moisture than transformer oil does. Acids are formed in lectronol during this adsorption. The process accelerates with increasing temperature. However, E_{br} does not drop below 0.12 MV per cm, at 60 Hz and 25 C, even for significant humidity.

Inspite of oxidability of this liquid, neither sedimentation nor perceptible increase of dielectric losses was observed at 70 C during 200 days.

5-4. Development of slip charges on the contact surface of transformer oil and air

Regularities in overlap of solid and liquid dielectrics as well as solid and gaseous ones over the contact surface can presently be considered well recognized. These problems have been presented quite extensively in [85] and [198]. However, very little is known in literature about charges along the interface boundary of liquids and gases.

It is known that electric charges forming on the surface, for example, paraffin and glass, decrease the flashover voltage [199]. Electrification of the surface also takes place when dielectrics obstruct the path of charges in the air [200] and [201]. It will be shown below that such charges play an important role also in flashover of liquids and gases over their contact surface.

It can be noted that a formula for flashover voltage, derived from a consideration of a substitution circuit with constants distributed at lead-in insulator, can be applied to liquid dielectrics in some particular cases [202].

Some empirical material concerning regularities in the discharge process over the contact surface of transformer oil and air is presented in [203].

The tests were conducted at room temperature in the air with relative humidity about 55%. Transformer oil of high purity was poured in a circular brass bath (a pan) 110 cm in diameter, at the level of 1.8 cm. Pulsating voltage was applied to a steel edge or a brass disc with smooth edges, 10 cm in diameter. The electrode was placed in contact with the oil surface at the center of the oil pan. Voltage was recorded and measured by means of a high-voltage cathode oscillograph, and discharges were photographed in a dark room. The bath served as the other electrode.

It has been shown that values of flashover voltages at the positive edge are greater than those at the negative one (see Table 36). The opposite situation occurs for breakdowns over air gaps in the case of an edge and a plane.

In order to have conducted a flashover only in the air for the negative edge, a voltage of about 9.5 kV per centimeter of the gap was necessary. However, in the case of contact between the transformer oil and air (for l equal to 55 cm), about 2.3 kV was applied over a unit length, while 2.8 kV per cm was the value for the positive edge. By this means, more favorable conditions for the development of sliding discharges as compared against breakdowns of air gaps with the same length and for the same electrodes.

Table 36

Values of flashover voltages over the contact surface of transformer oil and air (L equal to 55 cm)

Form of electrode and its polarity	Flashover voltage, kV
Positive edge	147 - 156
Negative edge	118 - 138
Positive disc	160 - 165
Negative disc	140 - 145

Photographs of discharges have indicated that the channel has a herringbone structure for a positive electrode (see photograph 1, Fig. 82). In the photographs, the letter A is assigned to the metallic rod to which voltage was supplied. Either edge (ph. I and II) in some cases or brass disc D (ph. III and IV) in others was fastened on the end of the rod. The edge and the disc were contacted to the surface of the transformer oil poured into a pan with sides m (phto I). The image of the discharge channel in oil is denoted by σ.

Aside from the herringbone structure, discharge channels had various zigzags, and even some "jumps" away from the contact surface towards the air in individual cases (see photo III). Such peculiarities were not observed for the layout with a negative electrode.

Oscillograms have contributed to the finding that the duration of the formation of the discharge in the case of a negative edge is served times smaller than that for a positive edge. The applied voltage was decreased by some 20 percent; i.e. after a well-conducting bridge had already occurred; which corresponds to 3×10^{-7} seconds for the negative edge (see Fig. 83) or 2×10^{-6}

seconds for the positive edge. All this information substantiates the assumption that the development of discharge from a positive edge occurred under the influence of some counteracting factors.

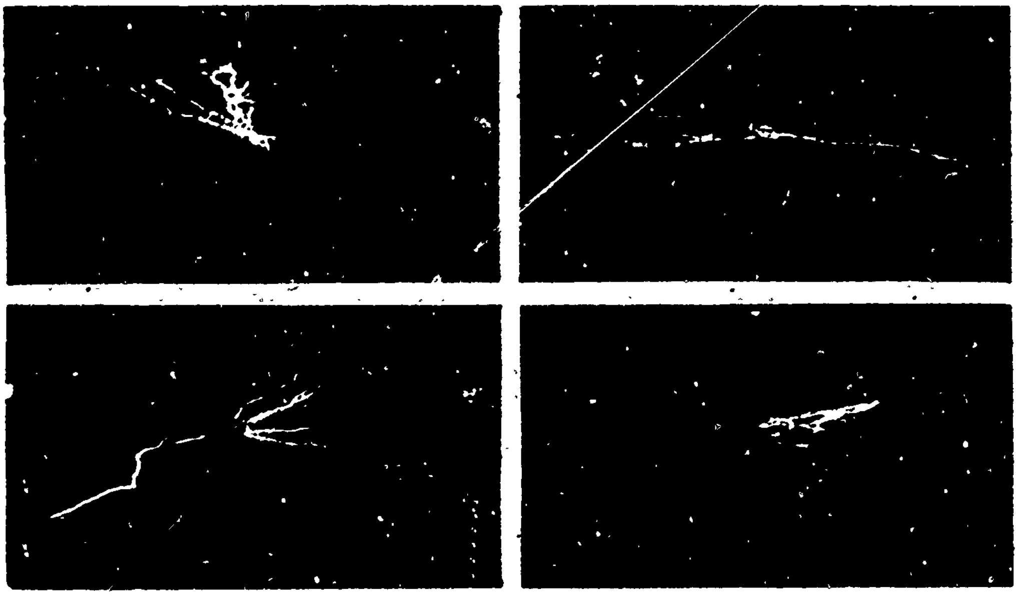


Fig. 82. Photographs of sliding discharges over the contact surface of transformer oil and air
I - discharge from positive edge A contacting the surface of oil; II - the same, but from positive edge; III - the same, but from positive disc D; IV - the same but from negative disc D; m - the end of the pan

In order to explain the specified peculiarities one should pay attention to the character of the formation of streamers from the positive edge during the formation of discharges. Fig. 84 shows a photographs of flashover on the surface of photographic paper in the case of pulsating 54·kV voltage and 6-cm distance from the edge to the plane [204]. The photograph shows that numerous streamers form at the edge (see ПО in Fig. 84) and occupy quite a large space. Flashover is executed within one of them. Such a property is caused by various mobilities of positive ions and electrons, as was already mentioned. At the beginning of impact ionization electrons flow to the edge and form a narrow stem of positive ions. During the subsequent ionization,

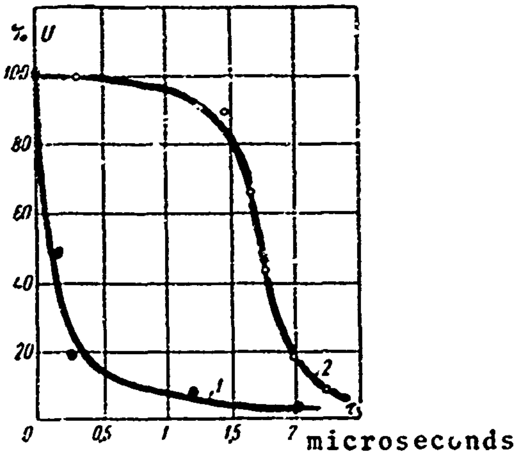


Fig. 83. Decreasing voltage for the formation of discharge over the contact surface of transformer oil and air as a function of time
1 - negative edge; 2 - positive edge

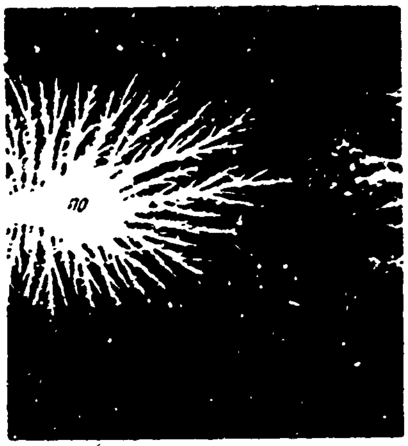


Fig. 84. Sliding discharge from the positive edge (ПО) over the surface of photographic paper; the plane being the other electrode.

electrons are poured into this stem, and a narrow conducting projection is formed. The projection can grow towards the plane maintaining sharp inhomogeneity of field between electrodes over the whole time.

Oscillograph recording has also shown that the formation of the basic arc over and perceptible decrease of the applied voltage start not immediately after the pulse height has reached the maximum value, but rather with some delay of about 4 microseconds. Numerous low-power streamers (they could not be taken in photographs) should also arise from the positive edge during this time. Ending up at the oil surface, they bring about non-uniform surface electrification and make the formation of the basic sliding discharge difficult. Therefore, zigzags are formed at the channel, which can point partially in the air.

Electrification, of course, occurs also at the place where the edge touches the oil surface. For a significant surface density of charge and acute inhomogeneity of the electric field, the development of flashover occurs for relatively small voltages applied.

Streamers are not formed during the delay time in the case of a negative edge, and preliminary electrification of liquid does not occur. Thus the sliding discharge is formed in more favorable conditions than in the case of lower voltages and during shorter time.

The influence of such low-power streamers is most pronounced when the edge is located above the grounded pan with transformer oil. During these tests, the edge was suspended over the center of the pan at various distances from the oil surface. Pulsating voltage of various polarity was applied to the edge. Discharges were recorded by means of photographs and oscillograms.

From bibliographical sources it is known that, edge and plane cases, a streamer always begins its development from the edge, independently of the polarity of the latter [205]. Therefore, it should not make any difference to the expanding streamer what the situation is at the plane. It should not "pay attention" to a thin layer of transformer oil over the plane until it approaches it very closely. Then, either oil breakdown, flashover on the contact surface, or stopping of the breakdown would take place.

However, tests [203] have shown that such a flashover development happens only from the negative edge. When approaching the surface, the discharge channel changes its trajectory at almost a right angle and continues developing over the contact surface of oil and air. Consequently, the breakdown of the air gap and surface sliding occur in this case.

These discharges are shown in photographs I and III, Fig. 85. Discharges propagate from point A, where the edge ends, pass toward oil surface M, and then reach the edges of the pan, M. Discharge images in the oil are seen at points B. The form of discharge channels is best distinguished by these images.

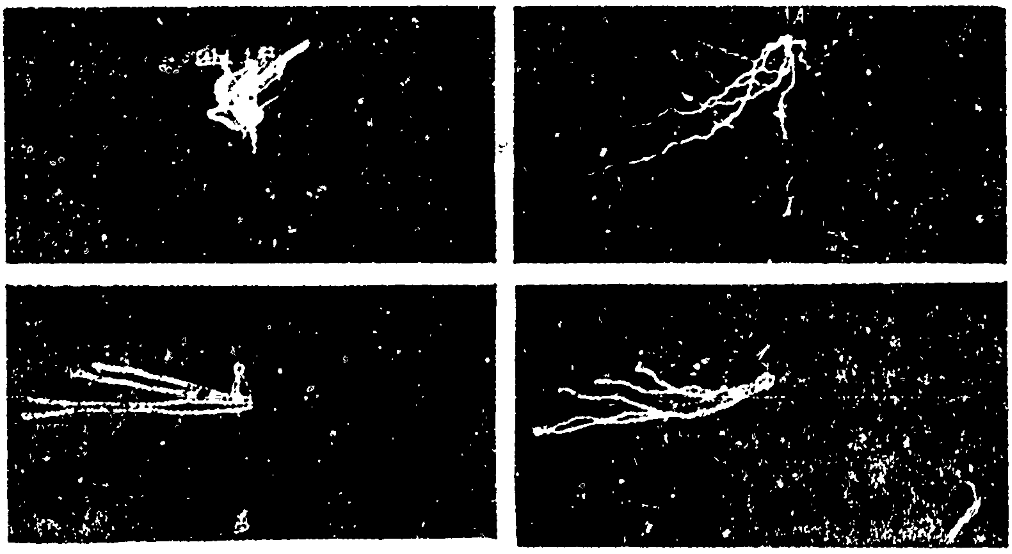


Fig. 85. Discharges from the positive and negative edges for their distance l from the surface of transformer oil
I - negative edge; l equal to 15 cm; II - positive edge, l equal to 20 cm; III - negative edge, l equal to 8 cm; IV - positive edge, l equal to 8 cm.

Quite a different picture is observed for discharges from the positive edge. Almost all discharges are oriented towards the edges of the bath but not towards the surface of the transformer oil, even if the edge is located only few centimeters away (see II and IV, Fig. 85). The surface of the transformer oil is located at mid-length AB. Only a breakdown of the air gap occurs in this case. It should be noted that if there were no transformer.oil, discharges from the positive or negative edges would always be oriented directly towards the central region of the pan.

For the positive edge, a portion of streamers formed during the static delay time of the flashover reaches the ends of the well-grounded pan. Electrons penetrate the narrow channel at the side of the ground and stimulate the formation of the reverse discharge. A well-conducting bridge is formed. The narrow channel of thermo- and photo-ionization expands, and voltage decreases almost to zero, i.e. a flashover takes place. If a streamer ends at the surface of the transformer oil, the current through the narrow channel cannot increase and the discharge is damped if the surface electrification density at the contact place is insufficient for the continuous formation of the sliding discharge over the surface.

By this means, one of numerous streamers is a sort of prospector. It shows the path of the basic flashover. This gives us the impression that discharges from the positive edge are pushed away by the surface of the transformer oil.

In the case of a positive edge, the values of flashover voltages were determined only by breakdowns of air gaps. However, in the case of negative polarity, sliding over the interface is also added to such breakdowns. Since breakdown voltages of air gaps are bigger for the negative edge, and they are large in the case of the positive edge for sliding over the interface, the curves depicting flashover voltages as a function of the distance l over the surface of the transformer oil have the form of scissors (Fig. 86). The curves show that values of U for the positive and negative edge are equal where l is about 4.5 cm. For distances greater than l, values of U are greater for the negative edge, and for l less than l they are greater for the positive edge.

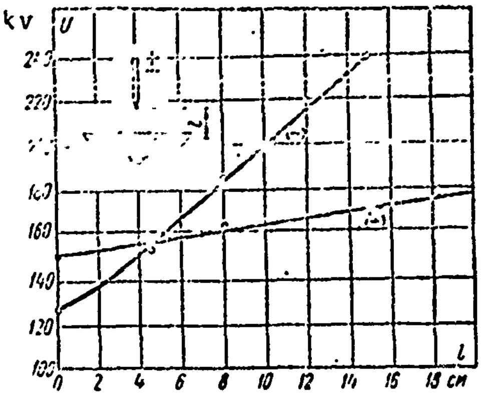


Fig. 86. Breakdown and flashover voltages as a function of distance for various polarities of a needle electrode located over a pan with transformer oil.

Chapter 6

PRE-BREAKDOWN PROCESSES IN LIQUIDS AND BREAKDOWN

6-1. Changes of conductance in stong electric fields

Regularities of the increase in current as a result of increased voltage applied is of great importance for understanding the breakdown formation mechanism. The investigation of these processes in liquid dielectrics had already started at the end of the last century. Tests with field strengths up to 300 kV per cm were then conducted. It was found that the current flowing through a gap between electrodes, 1 to 3 mm long (1), depends upon the character of the liquids, length 1 and the applied voltage [206]. A little later it was discovered that the magnitude of the current also depends on the character of the gas in the electrodes [207]. With regard to sources of current carriers it has been shown that the greater portion is coupled through its origin to external ionization radiation [155 and 156]. Based on results of further tests it was concluded that current in insulating liquids depends on the degree of purity, temperature, the geometry of the electric field, and the electrode material, but does not depend upon the external pressure over the liquid [208].

According to [209 - 211] impact ionization processes begin developing in liquids with increasing voltage of the applied field, and the current increases, in the same way as in gases. The volt-ampere characteristic of very pure liquids is essentially the same as that of gases (see Fig. 75); Ohm's law is satisfied for small field voltages, then the region of current saturation appears, and finally it increases sharply ending with breakdown. The saturation section vanishes in the case of low-impurity liquid dielectrics. However, further tests have shown that relationships I = f(E) of that kind are not observed very frequently. The saturation region is usually lacking. For instance, it has not been observed in pure isoctane [7]], well-purified xylene [110], and certain liquid hydrocarbons [9]]. In works [9]] and [110] it was concluded that the current increase in liquid dielectrics in strong fields takes place with a considerable contribution of cold-emission electrons from the cathode.

According to the data of [212], the predominant current increase mechanism in toluene with increasing E is the thermal emission of electrons from the cathode without impact ionization. Basically the same conclusion, although with some changes and modifications, has been drawn by the authors of [213] and [214]. However, they did not study the influence of the length of the gap between the electrodes, and their data is insufficient to infer the absence of impact ionization. The thermal-emission mechanism of the current increase is also reported in [215] and [216].

A slightly different conclusion has been presented in work [16]. Aside from thermal emission, impact ionization is also considered in that work. The author of works [217] and [218] assigns the nonlinear current increase to the dissociation of liquid molecules rather than to additives and ionic complexes. This conclusion, however, cannot be regarded as substantiated since a fairly large amount of energy (about 10 EV) would be necessary for that sort of dissociation.

When comparing the foregoing against the data of paragraphs 4-3 and 4-4 one can notice the apparently different treatment of the current increase mechanism. The condition of the surface of electrodes would play a decisive role in one case (emission of electrons from the cathode), the impact ionization in another, and both factors in still another case. With regard to this one should be aware of the fact that the electrode material does not affect the current magnitude in the case of small distances between electrodes [99].

It can be assumed that merely a single current increase mechanism in strong electric fields does not exist. For large gaps between electrodes, the growth of current is apparently determined by impact ionization in the most part, while processes in electrodes play a decisive role for small gaps.

Certain peculiarities in the increase of current in individual liquids can be assessed from the curves in Fig. 87 [110] for l equal to 0.57 mm. Very pure xylene was vacuum-distilled two times; heptane and chlorobenzene were distilled in air and in a vacuum. Plane electrodes of stainless steel had protective rings. The measurements were conducted at approximately room temperature.

For field strengths exceeding a certain critical value E_0 it has been found that a sharper increase of current takes place and that the magnitude of E_0 should characterize the given liquid to a certain extent. Corresponding values of E_0 are presented in Table 37.

Judging by the tabulated material, values E_0 are relatively small in strongly polar liquids. Causes of the steeper increase in current for $E>E_0$, are usually assigned to the beginning of impact ionization. It is little likely that a certain portion of this growth is related to the increased ion mobility. To prove this one can make use of curves in Fig. 88 presenting the relationship $I = f(\sqrt{E})$ for liquid (23°C) and solid (0°C) gasoline and l equal to 0.076 cm [218]. Electrodes of degassed nickel were used in the tests. The curves in Fig. 88 have almost the same form. If the mobility of ions increased in liquid gasoline with increasing E, the curves would diverge at a certain voltage E with increasing E, the curves would diverge at a certain voltage E greater than E_0.

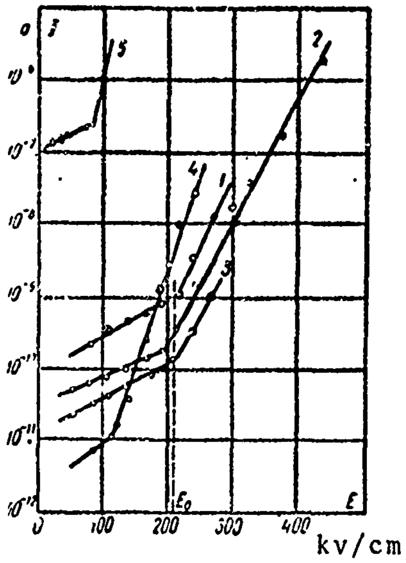


Fig. 87. Current as a function of the voltage of field applied at various temperatures t. 1-highly purified xylene, t=80°C; 2-the same at t=0°C; 3-the same at t=-20°C; 4-purified heptane; 5-purified chlorbenzene

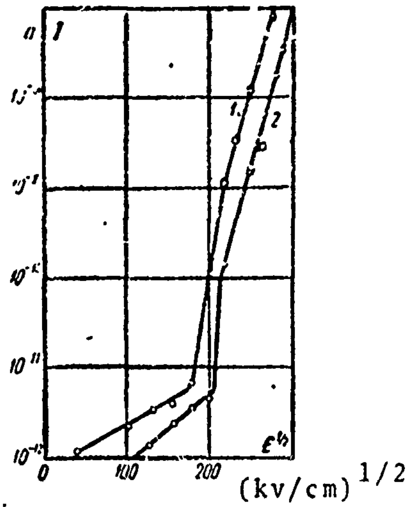


Fig. 88. Volt-ampere characteristics of gasoline; the gap between electrodes = 0.076 cm. 1-liquid gasoline; t=23°C; 2-solid gasoline, t=0°C

Table 37

Values of E_0 for some liquids

Liquid	Dielectric permitivity	Critical voltage E_0 mv/cm	
		After Walter and Inge	After Nikmadse
Xylene	2.3	210	---
Toluene	2.2	---	110 - 120
Heptane	1.9	110	---
Chlorogenzene	4.0	80	85 - 100
Nitrobenzene	32.0	---	<50

From curves in Fig. 87 and data of Table 37 one can conclude that voltage E_0 for the same liquid does not depend upon temperature. However, the steepness of current growth for $E>E_0$ depends on individual properties of liquids since, apart from impact ionization, it is the capture of electrons by molecules, the excitation of the latter, and recombination of charged particles which also begin to play an important role.

To date, minimum gaps between electrodes are unknown for which the specified processes determine the course of characteristics $I=f(E)$ for various liquid dielectrics. These problems have nto been explored yet. Only some remarks are available as to regularities of current increase for voltages $E>E_0$.

For instance, one can pay attention to the curves in Fig. 89, drawn for measurement data concerning currents in transformer oil at various temperatures [219]. The data refer only to the range $E>E_0$ or to a portion of the characteristic behind point B in Fig. 75. Based on these curves one can write the following for the I versus E function:

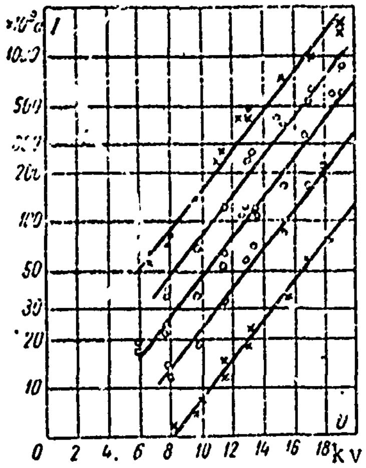


Fig. 89. Current as a function of pure transformer oil at various temperatures.

$$I = I_0 e^{cU} = I_0 e^{cEl}. \qquad (27)$$

It has been discovered that the power factor of (27) does not depend on temperature, and therefore it can be assumed equal to $c'(E-E_0)l$ (see Fig. 89 and Table 37). As was shown in the preceding section, the magnitude of this coefficient in the air is equal to $c(E-E_0)^2 l$, with c equal to 1.2 and $E_0=22.9$. From a comparison it follows that the growth of current under impact ionization in liquids develops laes rapidly than in air, due to the capture of free electrons by molecules. Negative ions are formed during this capture [44].

In theoretically substantiating the decrease in the intensity of ionization in liquids one can use an equation derived for the case of impact ionization and the capture of electrons by gas molecules [142] and [220].

Let us denote the number of electrons in 1 cubic cm. of liquid as n, and their velocity of motion as v. The amount of negative ions in 1 cubic cm. is assumed to be N, and their velocity is assumed to be V. Moreover, let us assume that the number of pairs of charge carriers, created by one electron during the collision along 1 cm. of path is equal to α', while the number of electrons captured along this section by neutral molecules is ε'.

For a uniform electric field one can write the following for the changes of nv and NV over length x:

$$\frac{dnv}{dx} = nv(\alpha' - \varepsilon'); \qquad (28)$$

$$\frac{dNV}{dx} = nv\varepsilon'. \qquad (29)$$

In assuming the cathode to be the source of electrons one obtains the following solution to these equations:

$$nv = n_0 v e^{(\alpha' - \varepsilon')x};$$

$$NV = n_0 v \frac{\varepsilon'}{\alpha' - \varepsilon'} \left[e^{(\alpha' - \varepsilon')x} - 1 \right].$$

The overall flux of charged particles at the anode (x=1) will be the sum

$$Z = (nv + NV)_{x=l} = n_0 v \left[\frac{\alpha' e^{(\alpha' - \varepsilon')l}}{\alpha' - \varepsilon'} - \frac{\varepsilon'}{\alpha' - \varepsilon'} \right]. \qquad (30)$$

A formula for current density can be obtained fsom equation (30) by multiplying Z by the elementary charge

$$J = J_n \left[\frac{a' e^{(a'-\varepsilon')l}}{a'-\varepsilon'} - \frac{\varepsilon'}{a'-\varepsilon'} \right],$$

where J_n is the initial current density at the cathode (x=0).

The constants a' and ε' can be determined from test data for current as a function of the distance betwwen electrodes. Let us introduce the notation

$$J_n \frac{\varepsilon'}{\varepsilon'-a'} = A; \qquad (31)$$

$$J_n \frac{a'}{\varepsilon'-a'} = B. \qquad (32)$$

Then we obtain the follosing for current:

$$J = A - Be^{-\mu l}, \qquad (33)$$

$$J = A - B = J_n. \qquad (34)$$

Values of μ can be calculated by the slope of empirical curves I=f(l) as follows:

$$J - J_n = B\left[1 - e^{-(\varepsilon'-a')l}\right]$$

and

$$B = \frac{J - J_n}{\left[1 - e^{-(\varepsilon'-a')l}\right]}.$$

The saturation current J_n is found empirically. On the basis of equation (34) one can easily determine A/B=ε/a', by this means, the absolute values of the ionization factor a' and adhesion ε' can be calculated by making use of their differences and ratios.

Fig. 90 shows curves for the dependence of currents in nitrobenzene versus the length of the inter-electrode gap, l, for various E. The calculated points in Fig. 90 are marked with flags. Parameters B,A,a' and ε' can be determined by using these curves. Their numerical values for nitrobenzene and mineral (transformer) oil are compiled in Tables 38 and 39).

It has been shown that the growth of a' and ε' in notrobenzene starts at smaller E than, for instance, in toluene and transformer oil. This is apparently due to the difference in the chemical

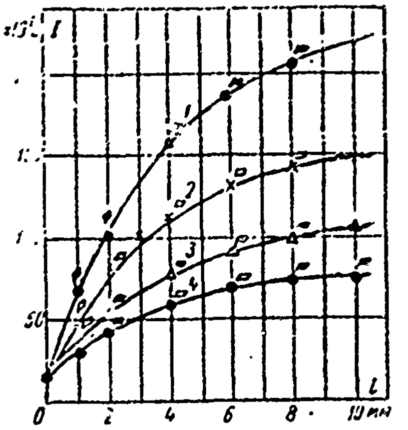


Fig. 90. Current in nitrobenzene for various interelectrode gaps and some field strengths

1-E=65kv/cm; 2-60kv/cm; 3-55 kv/cm; 4-50 kv/cm.

compositions of the liquids compared. ε' is greater than a' for fairly small field strengths, but the sign of the inequality is reversed after E has reached some E'. The increase of a' along with E confirms the presence of impact ionization in the liquid.

For the case of small interelectrode gaps, the processes of impact ionization become promounced only for very great field strengths. For example, the processes could be observed for E greater than 0.8 mv/cm in highly pure n-hexane if the distance between the sphere and the liquid was several tens of microns [215]. The numerical material obtained in those tests is presented as a series of curves in Fig. 91.

Table 38

Constants μ, B, A, a' and ε' for various E in nitrobenzene

Constants	Field Strength E, kv/cm			
	50	55	60	65
μ	2.94	2.85	2.75	2.72
$B \cdot 10^6 a$	66.00	95.00	146.00	220.50
$A \cdot 10^6 a$	80.00	109.00	160.00	234.50
ε'/a'	1.21	1.15	1.09	1.06
a'	13.90	19.00	29.00	41.80
ε'	16.84	21.85	31.75	44.52

If one had considered exponential curves accounting for a spherical emitting surface (sphere), the function I=f(E) would be rectilinear without the effect of impact ionization. In fact, such a relationship was observed up to E = 0.8 mv/cm. It breaks off for higher E. The author of work [214] therefore assumes that for E exceeding 0.8 mv/cm impact ionization starts in n-hexane for the specified l. the breakdown strength of the liquid was 1.55 mv/cm for l equal to 25 micrometers.

Table 39

Constants μ, B, A, a' and ε' for various E in mineral oil

Constants	Field Strength E, mv/cm			
μ	10.99	7.00	5.10	4.05
$B\cdot10^{10}a$	17.25	73.00	201.00	359.00
$A\cdot10^{10}a$	25.75	81.50	209.50	367.50
ε'/a'	1.49	1.11	1.04	1.02
a'	22.40	60.00	121.20	184.00
ε'	33.39	67.00	126.30	188.00

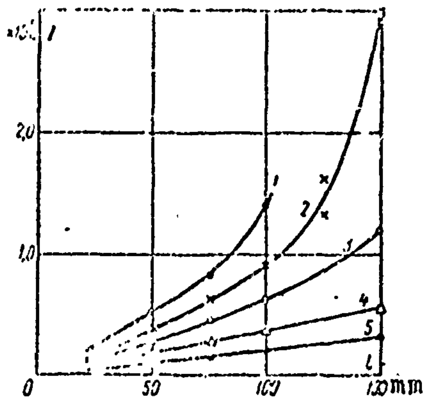


Fig. 91. Current in n-hexane as a function of the distance between electrodes for various E.

1- E=1.2 mv/cm; 2- 1.1 mv/cm; 3- 1.0 mv/cm; 4- 0.8 mv/cm; 5- 0.6 mv/cm.

On the basis of material obtained it was concluded that the function I=f(E) satisfies the equation of thermal emission if electrodes have been machined thoroughly. However, just the reverse statement has been made in work [147]. According to data of [91] even for highly refined n-hexane, the function I=f(E) basically satisfies the equation of cold emission.

It should be noted therefore that even though the volt-ampere characterists for very small l are determined by the state of the surface of electrodes, in principle, conclusions as to wheter characteristics I=f(E) obey equations of cold emission or thermal emission should actually be treated with great caution.

It was mentioned earlier that, in the case of direct voltage, current decreases rapidly over the studied period of time, about one minute. At this point it sculd be noted that the speed of this decrease is apparently affected by the chemical composition of the liquid and depends on methods of purification, as well. It is also possible that a certain role is played by length l, and the applied field strength. For example, they pointed out in work [221] that the same well-purified n-hexane for l equal to 0.024 cm and E about 0.06 mv/cm is characterized by a decrease in current for about five minutes.

What kind of relationship I=f(E) is observed for short rectangular pulses? Some information about this problem can be found in [158]. The authors of that work measured currents in n-hexane by using a system similar to Shering's bridge with a short pulse transformer. However, more detailed and interesting data were obtained in work [221] for the same n-hexane studied in the system presented in Fig. 92. U_0 denotes an applied voltage, C_1 the capacitance of electrodes of the liquid studied, R_1 its resistance and C_3 capacitance in the circuit of electrometer Э.

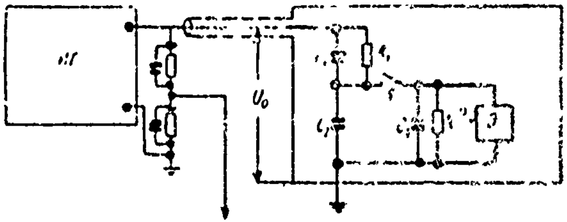


Fig. 92. System for measuring of currents in the case of short rectangular pulses.

Plane electrodes of stainless steel with bent edges (Rogovskiy's, electrodes) were used in the measurements. A rectangular pulse was applied to the circuit of R and C, and charge was created in capacitance C_2 with very good insulation; the charge was measured with electrometer Э after S had been switched on.

A desired resistance was calculated by the formula

$$R_1 = \frac{C_2 \tau U_0}{U_1 (C_1 - C_2)(C_2 - C_3)}, \tag{35}$$

where τ is the duration of pulse

U_1 is voltage at C_2.

It has been shown that current flowing through n-hexane, for short pulses, is several orders of magnitude larger than a steady current under constant voltage. The magnitude of this current does not depend upon the time that voltage was applied within the range of 1 microsecond to 1 millisecond. The use of such a flat section for U_{br} is proposed within more or less the same interval of expositions on the curve in Fig. 36.

Measurements of R_1 were conducted for various E and l (Fig. 93). The dotted curves denote identical field strengths on the studied object. Below the field strength E_1 = 1.2 mv/cm, values of current densities remained almost independent of length l within the range form 0.001 to 0.024 cm. Increasing current was, however, observed with increasing l for l greater than 1.2 mv/cm. This has also been assigned to impact ionization.

Work [221] notes the fact that random breakdowns in n-hexane occurred during the measurements also for E = 0.5 mv/cm. The current magnitude increased greatly after such breakdowns. Increased current was observed also when a liquid was substituted by a new portion. The replacement of electrodes or a good machining of old ones was necessary to maintain the former state.

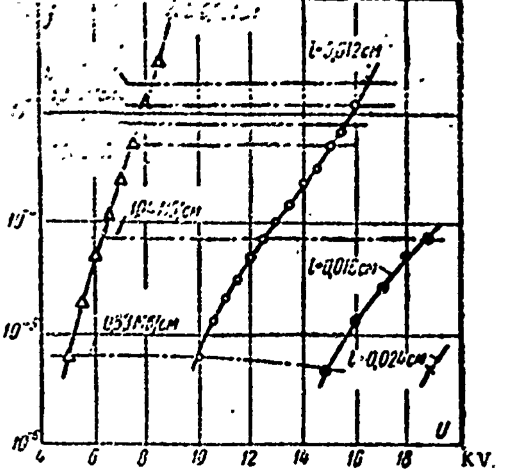


Fig. 93. Current density as a function of voltage in n-hexane for various gaps between electrodes, 1_x. Pulses are 5;3;and 1.5 microseconds.

Near breakdown voltage a large amount of energy (about 10,000 W/cm^3) is emanated in the gap between electrodes. Based on this finding, the authors of [221] consider that before breakdown a liquid can begin evaporating and liberating gas bubbles from which bridges between electrodes would form. At this point, however, one should pay attention to the duration of the action of voltage. The formation of bubbles is questionable in the case of short pulses.

By this means, in the case of short rectangular impulses and small gaps between electrodes, the processes of impact ionization in well-purified n-hexane are pronounced for higher field strengths (1.2mv/cm) than for direct voltage (0.8 vm/cm). But when do the breakdowns for 0.5 mv/cm form under such circumstances? If they do it without impact ionization and only due to cold emission of electrons, then a significant field intensification should be expected at the insulating cathode film. This could happen due to the contribution of positive ions and only if voltage were on for a longer time. Hence, this is not compeletely clear.

It is well-known that a strong motion begins at certain insulating surfaces in the case of great field strengths. This motion was subject to special investigations [222]. The mechanism of this phenomenon has not been discovered yet. Similarly, no fully-reliable data are available on the degree of this influence upon the relationship between I and E.

By solving equations of electro-dynamics and hydrodynamics (the Navier-Stokes equations) the authors of [223] have shown that a mobile medium must not be stagnant in an electric field. The velocity of a medium is small only for very weak fields and a small specific conductance. From an analysis of the obtained data it follows that for significant E the overall electric conductivity of a moving liquid should be basically determined by the convective motion of charged particles and displacement flows. The current should be proportional to the cube of the applied field strength in the case of laminar motion through the inter-electrode gap, or to the square -- for turbulent motion.

According to data of [91], current and applied voltage in n-hexane are interrelated linearly in the system with corrdinates being $\sqrt[3]{I}$ and U. This is explanied in work [224] as the result of the laminar motion of the liquid during the measurement of currents. The relationship can also be linear for transformer oil if one uses coordinates $\sqrt{I}$ and U [85]. According to [224], this is possible only for spontaneous turbulent motion of transformer oil.

Following this concept, neither chemical composition of liquids, impact ionization, the influence of electrodes, nor additives etc. should be taken into account when explaining the nonlinear relationship I=f(E). However, empirical data imply the importance of those factors. One should measure currents for small E_x and forced laminar or turbulent flow of liquids if one aimed at explaining why the specified factors cannot create the nonlinear relationship by themselves.

Based on data on the beginning of ionization processes and the influence of the condition of the electrode surface one can apparently clarify very sophisticated relationships with "light" and "dark" points.

"Dark" is the adjective given to the current that can be measured in a dark room without the influence of light on the object tested. It increases drastically in certain liquid dielectrics and insulating mixtures with increasing E. The dark current can be added to a significant "light" component if a liquid is subject to ultraviolet light radiation from a quartz lamp. The overall current will then flow through the gap studied. Under reiterated measurement, the current will increase in a way identical to this before irradiation, i.e. the "light" component remains almost unchanged.

For example, a solution (10 moles per liter) of antracene in pure hexane was tested. The current was stabilized soon after ultraviolet radiation by means of a quartz lamp. This process lasts several hours in many light-adsorbing liquids. Separate "dark" and "light" components were measured along with f(E) [3]. It has been found that the "dark"current increased very much for increasing E, but the photoelectric current ("light" one) does not depend on E. It remained constant up to about 300 kv/cm (Fig. 94). No exponential increase was observed, as could be anticipated according to the theory of impact ionization.

Solid curves in Fig. 94 were drawn according to test data obtained during measurements of photocurrents for l equal to 0.5 mm (circles) and for l equal to 1 mm (crosses). The dotted curves show values of currents calculated under the condition of

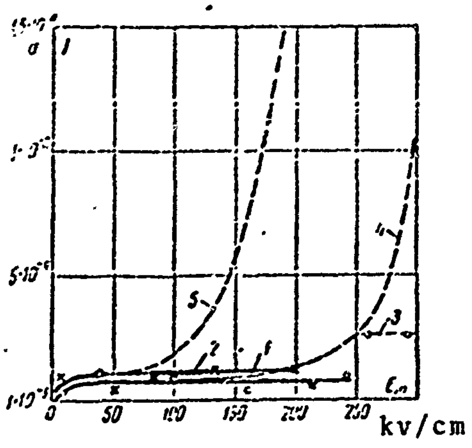


Fig. 94. "Light" current in a mixture of n-hexane and anthracene as functions of the applied field voltage.

1- test curve for l=0.5 mm; 2- the same for 1 mm; 3- the upper limit of increasing current during tests; 4- calculated curve for l=0.5 mm under impact ionization; 5- the same for 1 mm.

the existence of impact ionization.

Almost the same laws for the growth of "dark" and "light" currents have been found as a result of the study of degassed heptane [218]. Degassed and roughly cleaned molyldenum semi-spheres were used as electrodes.The increaed of "dark" current with increasing voltage was observed for E above 60 kv/cm.

It can be added that about the same character of relationship was also noticed in the investigation of certain semiconductors [225].

"Light" currents can usually be measured only in combination with "dark" ones. It has already been mentioned that increasing current with increasing E up to very high values can be determined by the state of electrode surfaces in the main part. If the same thing had taken place in the measurement of overall current, then the growth of the "dark" component could have been explained in terms of the emission of electrons, strengthened by the field of positive ions, which gathered in large amounts at the insulating film on the surface of the cathode with increasing E. Addition of the "light" component only increased the "dark" current. The condition of the surface of the cathode was almost unchanged, and thus there was no reason for a sharper increase of the overall current.

Several formulas have been proposed for the relationship of electrical conductivity or current on the voltage of the field applied. It has been assumed that some of them are suitable for both liquid and solid dielectrics. One of those formulas, similar to (27) is Pool's [226].

$$\sigma = Ae^{bE} \tag{36}$$

Tests have shown that this formula is really applicable for some liquid and solid dielectrics [227, 228, 229].

Frenkel has proposed a formula [153] with a slight modification based on the classical mechanism of the ionication energy of a polarized atom decreasing in an electric field E by a value $\Delta W = 2\sqrt{e^3E}$. According to this formula, conductance changes as

$$\sigma = \sigma_0 e^{\frac{1}{kT}\sqrt{\frac{e^3E}{\varepsilon}}}, \tag{37}$$

where e is the elementary charge, and ε the electron component of absolute dielectric constant equal to the square of the coefficient of refraction.

It has been shown that formula (37) can be used for a limited number of dielectrics. For some of them (mica), σ, changes according to (36) and afterwards it changes according to (37) after a certain increase in E [230].

The formula by Onsager [231] can also be quoted for the relationship in liquids. It was derived for the number of dissociated ion pairs, n, in a homogeneous solution after an electric field has been applied, as follows:

$$n = \text{const}\sqrt{\frac{J_1(4i\sqrt{-q})}{2i\sqrt{-q}}},\tag{38}$$

where J_1 is a Bessel function of the second kind,

and e_1 and e_2 are charges of ions, while the porducts e_1v_1 and e_2v_2 correspond to their mobilities.

The formula becomes simpler for small values of the absolute dielectric constant:

$$n = f(\varepsilon, T, E)\, e^{\frac{1}{kT}\sqrt{\frac{e^3E}{\varepsilon}}}.\tag{39}$$

Attempts were made to compare values σ calculated according to (39) and (27) against empirical data [232]. It has been found that the experimental relationship $\sigma=f(E)$ obeys formula (39) only on an order of magnitude. The dispersion of test data was large that the obtained data could be regarded as satisfying formula (27) as well.

In presenting the existing theories of the breakdown of liquid dielectrics we will point out a successful attempt of calculating E_{br} for carbon tetrachloride by formulas derived for crystalline dielectrics. Adaptations of that kind will probably prove expedient in the determination of σ in some individual cases. Therefore one should pay attention to another formula $\sigma=f(E)$ derived by Freilich [232] for crystalline dielectrics as well.

$$\log\frac{\sigma}{\sigma_0} - \frac{E^2}{E_{np}^2}\cdot\frac{W}{\Delta W}\cdot\frac{1}{e};\tag{40}$$

where E is the strength of the field applied;

E_{br} = strength of the applied field at the time when dielectric breaks down;

ΔW = difference of energies of the conductivity zone and levels of excitation;

$W = \frac{W_0+\Delta W}{2}$, where, in turn, W_0 is the energy between the major zone and the zone of conductivity;

$e = 2.713$;

σ_0 = conductance in weak fields.

A fairly good coincidence of empirical data for σ and those calculated by (40) has been found for black dried lacquer.

Thus, three different forms exist for formulas describing the relationship $\sigma=f(E)$. According to one of them, σ should increase exponentially with the index of $B\sqrt{E}$, and the third - the square of E according to cE^2. Simultaneously, it has been discovered that the change of conductance for some dielectrics with increasing E can be expressed by one of the specified formulas with a certain accuracy. But none of them can be regarded as universal. From this it may be concluded that the increase mechanism of σ with increasing E is different in various dielectrics.

6-2. Pre-breakdown Process in Liquids

The formation of breakdown in liquids usually occurs with a certain delay even if the appleid voltage is much larger than the minimum breakdown voltage [89]. This condition is a characteristic property fo liquds. In principle, this is not observed in gaseous dielectrics and many solid ones. The delay time of breakdown in very small spaces filled with a liquid is determined by their length l [56], machining of electrodes, and static factors [233]. The better the machining, the longer is the delay time [234]. This regularity is without doubt determined by the cold emission of electrons from the cathode.

The time period from the moment of reaching the breakdown value by the pulse height under the long action of voltage, to the beginning of the formation of breakdown or perceptible decrease of amplitude is commonly called the time of static delay. For gasses, for example, it is assumed that during this time a free electron will appear which can induce avalanches by impact ionization and, furthermore, progressive development of breakdown.

It has been pointed out in the preceding sections that the process of current increase before breakdown differs somewhat from the same process in gases, for voltages close to the breakdown voltage. A portion of the avalanche electrons is captured by liquid molecules, and those remaining are accelerated by the applied field. Under inelastic collisions, they consume the energy obtained from the field and excite vibrations of atom groups of complex molecules. This creates a kind of barrier preventing a liquid dielectric from breakdown under small E. Impact ionization starts only for field strengths close to the breakdown strengths. Problems arise as to whether the process of breakdown formation alsays develops progressively at the beginning of the ionization and what happens in dielectric during the time of static delay.

Some researchers consider that, as a result of the decrease of ionization energy due to the interaction of internal fields of molecules, individual acts of impact ioniaation in condensed phases occur fairly frequently even for rather low voltages of fields applied. If this were true, the concept of a free electron able to create an avalanche and to induce progressive formation of breakdown would become meaningless. Free electrons can appear in liquid at any time of static delay, but also at any time they can be captured by molecules or recombined. Based on this reasoning one can assume that the dynamic process of the breakdown formation during the static delay time occurs continuously but with the active participation of counteracting factors. Tests have confirmed this point of view.

The tests were conducted according to the scheme presented in Fig. 95 [89]. Voltage was applied from a pulse generator IG to a tested object B either directly (diagram a) or through a restricting resistance r_0 (diagram b).

During breakdowns of gaseous gaps it was observed that the occurrence of stepwise leaders or streamers in the spark gap is accompanied by a small but acute voltage decrease [235] and [236]. Based on data of [103] one could conclude that the same happens in liquids. Therefore, a high-voltage cathode oscillator was applied to record the pre-breakdown processes.

Before tests, transformer oil was purified with 30 percent fuming sulphuric acid. After washing it was vacuum-dried at 100°C and filtered. Castor oil was vacuum-dried also at 100°C and was filtered after cooling. Light fractions of xylene were removed during distillation. Electrodes were polished and heated at high temperature, also in a vacuum.

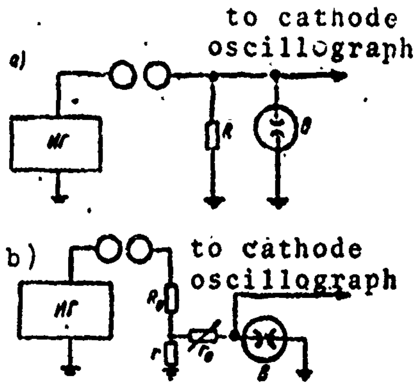


Fig. 95. Systems of tests of pre-breakdown processes.

Fig. 96 presents oscillograms recorded during the study of the specified liquids. Among them oscillograms I, II, and III were found by using system a (Fig. 95), while oscillogram IV was determined for system b. The period of calibrating sinusoidal oscillations on the abscissa axis of oscillograms I, II, land III is equal to $5 \cdot 10^{-7}$ sec. Explanations for the oscillograms are given in Table 40.

After switching on a voltage equal to the breakdown voltage, the static delay of breakdown in transformer oil lasted 30 microseconds (oscillogram I). During this time quite intensive processes of impact ionization were taking place with the simultaneous formation of small streamers, which can be judged by teeth 1,2,3, and 4 on the pulse wave of oscillogram I. The same has been noticed in castor oil in the case of positive edge (oscillogram III). In this case the occurrence of the first streamer has been observed earlier during the time of static delay equal to 50 microseconds.

By this time, intensive processes of impact ionization with the formaton of electron avalanches and small streamers take place in strongly heterogeneous fields during the pre-breakdown period. The occurrence of each streamer can be regarded as the beginning of the formation of breakdown. However, this formation was damaged several times by the intensive capture of electrons. A large amount of charged particles collected in the space between electrodes and complete breakdowns were finally formed. Since the occurrence of streamers has been observed for the positive edge as well, one may assume that their formation by the mechanism of impact ionization can develop without the cold emission of electrons from cathode, too.

Basically, the same phenemenon is observed in uniform fields (see II in Fig. 96). For E equal to 0.315 up to 0.35 mv/cm the breakdown of transformer oil was not formed despite the ionization processes during the pre-breakdown time were fairly intensive, as

Fig. 96. Voltage oscillograms during pre-breakdown time

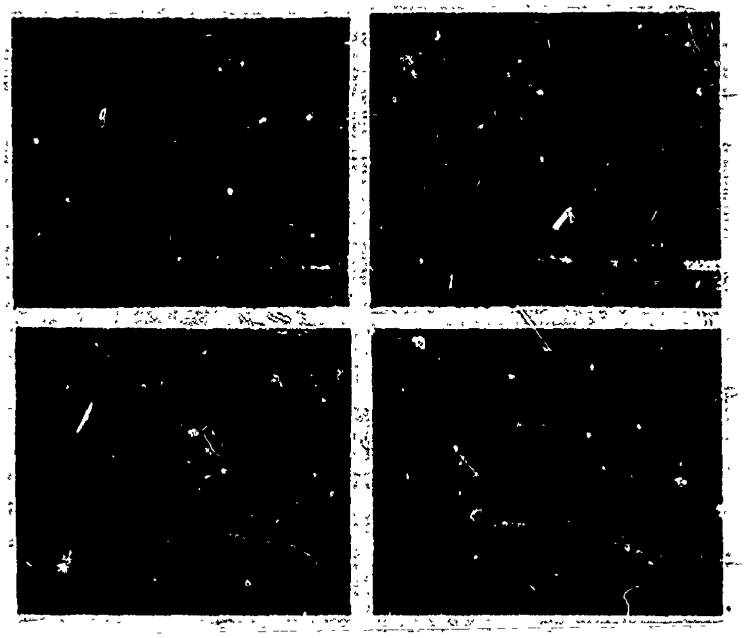


Table 40

Explanation to oscillograms in Fig. 96.

Ordinal numbers of oscillograms	Liquid	Electrodes	Gap between electrodes mm	Resistance limiting discharge current, ohm	Time from maximum amplitude of a pulse to the occurence of a first streamer or an avalanche of electrons
I	Transformer oil	Negative Steel Edge and Brass Plane	50	—	19,5
II	Same	Polished Brass Spheres 6.25 mm in diameter	10	—	0,5—3
III	Castor oil	Positive Edge and Plane	150	—	6,5
IV	Xylene	Steel Spheres 11 mm in diameter	0,2	$5 \cdot 10^4$	To maximum amplitude

well. The occurrence of streamers was noticed almost immediately after pulses had reached the highest amplitude at points 1 and 2. In photo II, several pulses are described, which are presented at 1 to 2 minute intervals to the same portion of the transformer oil. A very large amount of tiny dots representing very accurate, short-time decreases in voltage (see arrows) may be seen at the ridge of the pulses. In certain cases the interval between these depressions is equal to fractions of a microsecond at most. One can assume that such small oscillations of voltage have been caused by electron avalanches formed under impact ionization. Their duration was about 10^{-8} seconds.

Oscillogram IV in Fig. 96 was recorded for a limiting resistance of 5 millon ohms. The voltage of pulses was gradually increased to breakdown which occurred at E equal to 0.7 mv/cm, and for smaller voltage numerous partial breakdowns 1,2,...5 were observed even during the period of maximum amplitude during the time prior to breakdown cannot be recorded very easily, by means of an oscillograph. Weak and acute voltage drops are hardly legible for considerable density of blackness on a photographic plate, and deep cuts rarely appear.

There is information [237] about possibilities of the formation of weak electron avalanches in carbon tetrachloride , mineral oil, and some other liquids also under small alternating-field voltages (several tens of kilovolts per centimeter).

Luminescence is observed in transformer oil at places with large potentials [37]. According to data of [238] it is induced by the fluorescence of excited molecules of aromatic compounds, the traces of which always appear in transformer oils. The same luminescence is also observed in n-hexane containing small additions of anthracene. Very pure n-hexane does not become fluoroscent even for E equal to 1.1 mv/cm.

After [37], the presence of fluorescence in transformer oil indicates the existence of electrons with energy of several electron volts. These electrons are able to induce dissociation of complex hydrocarbon molecules with liberation of hydrogen or concentration of a gaseous medium; in the case of impact ionization they usually are a source of electron avalanches and small streamers.

Slightly different pre-breakdown processes were fixed during tests with distilled water. Oscillograms recorded for system a of Fig. 95 are presented in Fig. 97. The perioded of time-sinusoidal calibration oscillations on the abscissa axis of photograph IV is equal to $5 \cdot 10^{-7}$ seconds. The oscillograms are explained in Table 41.

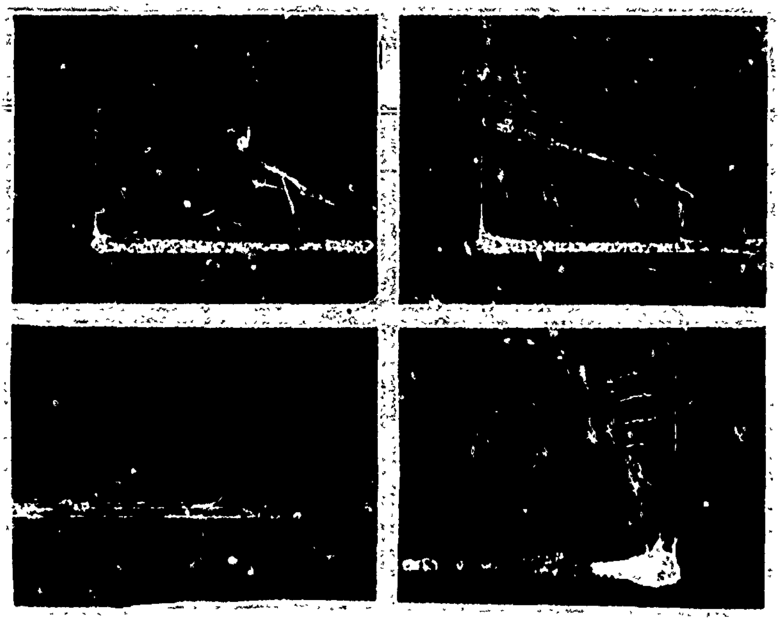


Fig. 97. Oscillograms of voltage changes during the pre-breakdown time and at the time of breakdown for distilled water.

Two lower oscillograms A in photograph I, Fig. 97, were recorded in the absence of any breakdown. The length of the pulse

Table 41

Explanations to oscillograms in Fig. 97.

Ordinal number of oscillogram	Form of Electrodes	Gap between electrodes mm.	Highest voltage amplitude kv	Voltage during the formation of breakdown kv	Delay time of the formation of breakdown, microseconds
I	Negative Steel Edge and Brass Plane	150	60—132	25,5—34,0	423—348
II	Same	100	77—115	30—43	202—180
III и IV	Positive Steel and Brass Plane	150	53—185	39—125	5—192

wave can be determined from them (343 microseconds). For a given capacitance of a pulse generator it has been determined by resistance R of the system a in Fig. 95. Pulses with the specified length were continuously applied to a tested object. With increasing voltage higher and higher current flowed through a tested section B; thus ever decreasing resistance r_1 of distilled water was switched on in parallel. The overall resistance was decreasing and the wave-length was being shortened. The breakdown itself formed for relatively small voltages.

For the negative edge, electrons and negative ions moved toward the plane during the breakdown delay time. As in the case of gasses, a well-conducting projection formed at the edge, and high potential was transferred into the gap. For a certain voltage, impact ionization strated at the plane and breakdown followed.

From oscillograms I and II one may see that increasing the pulse amplitude brings about only a small decrease of delay time, while the volue of U_{br}, for which the "failure" of voltage occurs, remains almost unchanged. This time decreases for small gap between electrodes. For example, the delay τ is about 202 microseconds (oscillogram II) for l equal to 100 mm and U equal to 77 kv, whereas it is about 423 microseconds (oscillogram I) for l equal to 150 mm and the same value of U. Such a great discrepancy can be explained in terms of the motion of negative ions toward the plane. The mobility of the ions seems to depend little or not at all on the field strength.

For the negative edge and plane, the minimum delay time of breakdown (about 5 microseconds) remains constant even for pulse voltages exceeding the smallest breakdown one more than three times (oscillogram IV). The static delay time vanishes in this case. The intensive process of teh formation of breakdown begins immediately after the voltage has reached the maximum value or even a while before. The time before acute drop of voltage can be called active delay.

The formation of a well-conducting bridge during the process of breakdown takes place in a certain sequence. This can be judged from sections a and b on oscillograms III in Fig. 97. At the beginning the electrodes are apparently connected through a low-power streamer with a small diameter. This time corresponds to the section of sharp decrease of voltage a. Temperature of the discharge channel increases very much. During the next time intercept the discharge channel expands gradually under the action of impact ionization, thermal ionizaiton, and photo-ionization. The process lasts over 10 microseconds (see Oscillogram III in Fig. 97). Additional data will be presented in the next section for this final stage.

It can be assumed that during the static delay time quite intensive impact ionization occurs, at least in some liquids, but free electrons are captured by molecules, and while forming breakdown is damaged for a certain time. Tests have shown that basically the same process occurs during the formation of breakdown of individual ceramic dielectrics and even air [239, 240, 241].

6-3. Variation of current before breakdown and the mechanism of breakdown

On the basis of certain test data on the function I=f(U) one could have assumed that with voltage increasing up to the breakdown value the current flowing through a tested liquid increases smoothly without any stepwise changes whatsoever. With regard to this, a characteristic curve is the volt-ampere one for pure transformer oil [93]. It was recorded for *l* equal to 1 mm (Fig. 98). For E about 0.17 mv/cm, breakdown occurred at the point indicated by the dotted curve. Judging by the course of the curve one can get the impression that the breakdown proved possible for a certain current equal to about $4 \cdot 10^{-6}$ A.

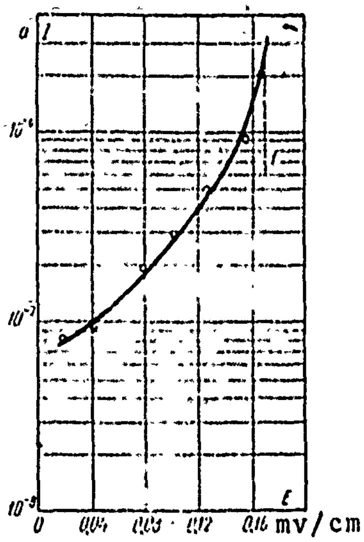


Fig. 98. Volt-ampere characteristic of transformer oil. Breakdown at point 1.

Acute increase of current before the moment of breakdown cannot be observed in highly purified n-hexane, either (Fig. 99). The distance between thoroughly machined electrodes was equal to some 10 micrometers in uniform field. The last measurement of current was possible for E equal to 1.045 mv/cm. Some deceleration in the rate of the growth fo current was observed for the field strength exceeding 0.4 mv/cm. The occurrence of impact ionization proved possible only for E greater than 0.8 mv/cm [147]. Before breakdown current was about $7 \cdot 10^{-12}$A. However, current is greater by several orders of magnitude at the time of breakdown, unless big limiting resistances are connected.

Then the question arises of when and how does such an increase develop.

Some information concerning this phenomenon can be drawn out from oscillograms of current I and voltage U in Fig. 100. They were recorded for the breakdown of a well-purified transformer oil. A 50 mm wide gap between a negative edge and plane was broken down. The period of time-calibrated, sinusoidal oscillations along the abscissa axis is 10 microseconds [242].

Oscillograph recording of current I was carried out for voltage U. The remaining oscillograms were recorded for lower voltages. The static breakdown delay time (a) was reduced. Any increase of current was not observed before breakdown, either. I_{max} is about 56A in oscillogram 1 at the time of breakdown. For about 3 microseconds current was increased by seven orders of magnitude (see Fig. 98).

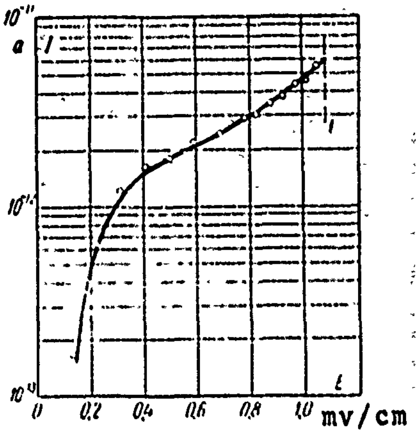


Fig. 99. Volt-ampere characteristic of well-purified n-hexane. Breakdown at point 1.

Fig. 100. Oscillograms of current and voltage during breakdown of well-purified transformer oil. Electrodes are sharp; plane.

Thus, one can add to the volt-ampere curves in Figs. 98 and 99 the remark pointing out that current increases stepwise by several orders of magnitude during a very short period of time during the formation of breakdown in n-hexane and transformer oil. The intensity of the process of impact ionization at voltage U_{br} is high enough to allow the capture of electrons by molecules not to be noise for the formation of a well-conducting bridge.

It has been said above that considerable deceleration in the growth rate of current is observed in n-hexane for E greater than 0.4 mv/cm (Fig. 99). Even greater deceleration was revealed for well-dried and filtered, light glycerine in both homogeneous and very inhomogeneous fields.. The relationship I=f(E) was determined by oscillograms of Fig. 101.

The experimental procedure is shown in Fig. 102 along with the volt-ampere curve developed according to oscillograms I in Fig. 101. The following notation has been used in Fig. 102: K- kenotron; S- measuring vessel, and R- current-measuring resistor.

Oscillograms I (Fig. 101) were recorded during the breakdown of the gap 0.5 mm wide between spheres, oscillograms II - for 1 mm, but between the edge and the plane. Oscillograms of voltage U were recorded without breakdown, but their maximum amplitude was very close to the breakdown value. The periode of time-calibrated, sinusoidal oscillations on the abscissa axis of oscillograms was equal to 44 microseconds.

The stepwise leader process of the formation of breakdown in oscillogram 1, Fig. 1 (Fig. 101) began about 550 microseconds after the applied pulse U had reached the highest amplitude; the stepwise character is not pronounced very much, however, for that slow time course. Any significant increase of current just before breakdown was not observed, either. This is clear for the ampli-

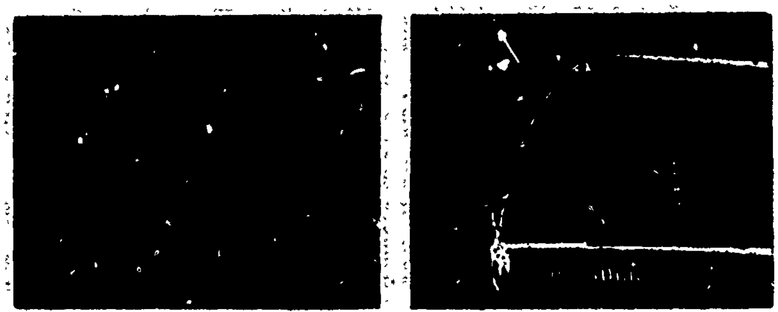


Fig. 101. Oscillograms of current and voltage for the breakdown of light glycerine

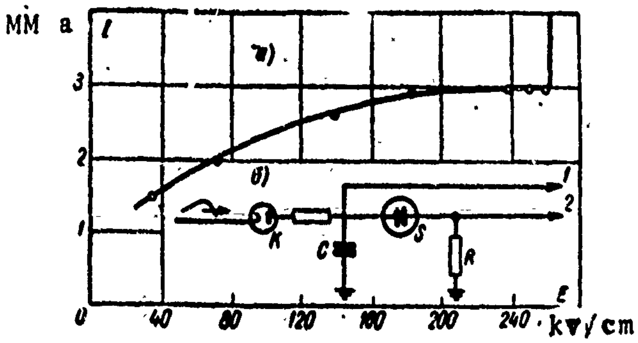


Fig. 102. Volt-ampere characteristic of light glycerine for 0.5 mm gap between steel spheres (a) and test circuit (b).

Table 42

Explanations to oscillograms in Fig. 103

Ordinal numbers of oscillograms	Form of Electrodes	Distance between electrodes mm	Maximum voltage amplitude kv	Breakdown forming voltage kv	Maximum current for breakdown A	Delay time of breakdown, microseconds	Period of calibration sinusoids on abscissa axis, microseconds
I II	Spheres	0,50	9,0	7,7	0,38	52,0	2
	Positive Edge and Plane	1,00	8,8 8,2	8,1 0,8	0,27 0,27	60,0 90,0	2
III IV	Same	[illegible]0,00	132,0	110,0	—	—	2
	Same	170,00	—	—	2,67 2,40	70,0 125,0	10
V VI	Same	170,00	100,0	75,0	106,0	5,0	10
	Negative Edge and Plane	110,00	115,0	50,0	68,0	198,0	44

tude of currents n for both spherical electrodes and a needle end plane. The bias current was perceptibly superimposed on conductance current only during the first 20 microseconds. It is accounted for in an analytical way in the derivation of the volt-ampere curve in Fig. 102.

The growth of pre-breakdown current in glycerine lasted up to E about 200 kv/cm. The saturation range occurs further and its setpwise growth takes place already in the formation of breakdown. Intensive impact ionization started only for voltages close to the breakdown ones. For smaller voltages, it was either slight for considerable capture of electrons by glycerine molecules, or absent.

From oscillograms in Fig. 101 one can see that high-frequency oscillations arise after breakdown, during sparking in glycerine. Their occurrence can be assigned to perturbations of equilibrium state in the well-conducting discharge duct. If for any reason, e.g. as a result of recombination, the current intensity diminished in the spark pattern, the difference of potentials on resistor R decreased, and that at capacitor C increased. Since the occurrence of impact ionization in the spark duct the current increased, then the voltage drop at R increased, etc. Apparently for this reason the process of the formation of breakdown has been a stepwise-leader one.

The increase of current was not observed before the breakdown in relatively small gaps in distilled water in a homogeneous as well as in a very inhomogeneous electric field. This can be inferred from oscillograms I and II of Fig. 103, recorded in the system shown in Fig. 102. The current flowing during the delay time of breakdown is denoted by I_2 in those oscillograms, while that for voltages little smaller than U_{br} are I_0.

The remaining oscillograms (III to VI) were found for the breakdown over longer spark gaps in distilled water, according to system a in Fig. 95. A steel edge and a plane were used as electrodes. Some explanation to the oscillograms is given in Table 42.

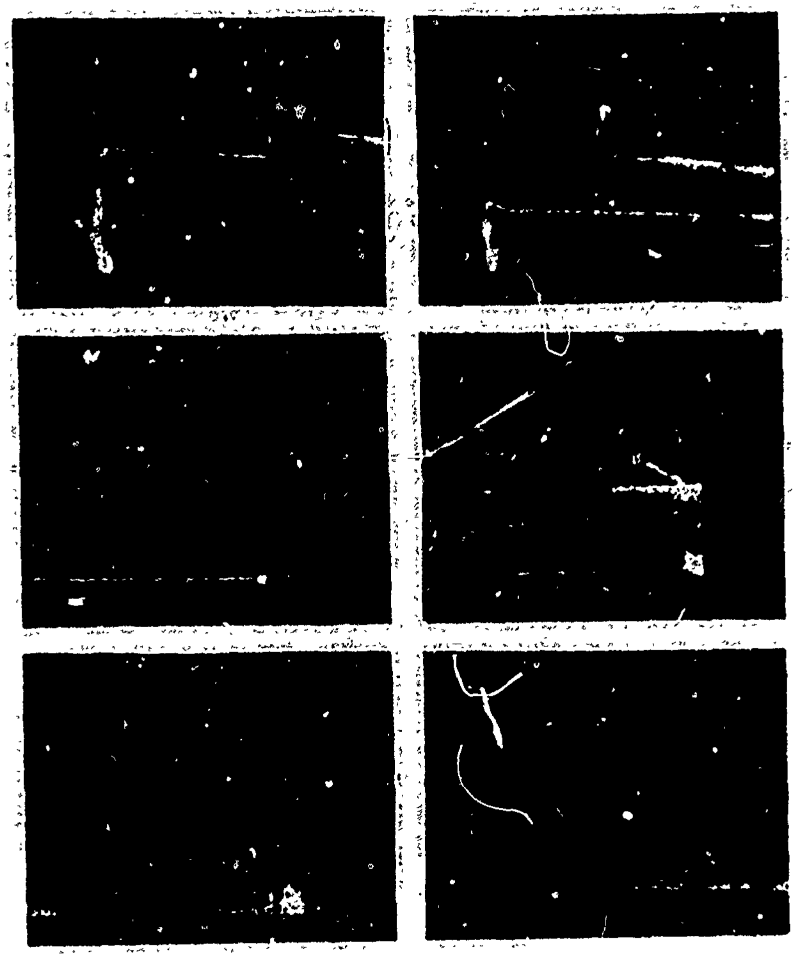


Fig. 103. Oscillograms of breakdown in distilled water, Period of time-calibrated sinusoidal oscillations along the abscissa axis of oscillograms is equal to 2 microseconds for I to III, 10 microseconds for IV and V, and 44 microseconds for IV -- A note: Oscillogram II is voltage-calibrated like oscillogram I.

During recording oscillograms I and II the discharge current was limited by means of resistance R equal to 120,000 ohms at the earth side. Voltage was recorded without disconnecting this resistance. Therefore, the amplitude of pulse did not reach zero during breakdown. The stepwise character of the growth of current can be acutely watched at by the presented oscillograms. Several oscillograms of current I and one for voltage U are presented in Fig. 1 (Fig. 103). The form of current steps hardly coincides with the corresponding voltage steps since recording was carried out twice: first the voltage was recorded, and then the current, during repeated breakdown.

Currents in patterns III and IV (Fig. 103) were recorded with limiting resistance r equal to 16 kilohms used at the earth side. It is not shown in the system 2, Fig. 95. For this r discharge currents have exceeded conductance currents without breakdown by a factor of about 3.

After applying voltage of about 123 kv to a positive edge and an earthed plane (for l equal to 200 mm) slow growth of current I began at the edge 8 microseconds after impact ionization (Fig. III). However, free electrons were being captured by water molecules apparently even prior to reaching the edge. A narrow, well-conducting projection was not formed at the edge, and further increase of current stopped after some 10 microseocnds.

In order to bring about the progressive development of breakdown the distance between electrodes was decreased to 170 mm. The most successful records of current at the time of breakdown were possible for 120 kv (oscillogram I_1 in Fig. IV) and 108 kv (oscillogram I_2 in Fig. IV). the 170-mm gap was broken down only after a triple supply of pulses with maximum amplitude 108 kv. Only conductance currents I_0 were recorded. Oscillograms IV allow watching at the laws of the progressive development of the stepwise-leader breakdown.

The time intercept before the acute growth of current in stepwise leaders B in Table 42 is conventionally denoted as the breakdown delay time. But from oscillograms IV one can well see that small streamers A increased and were damped during that time (70 to 125 microseconds) without completely bridging the electrodes. The current of each consecutive streamer of leader was a little higher than that of the preceding one. Such leaders were formed in large amounts. After 125 microseconds (oscillogram I_1) or 70 microseconds (oscillogram I_2) leader currents increased suddenly and very acutely (see B). Electrodes were, undoubtedly bridged. After damping of every low-power streamer (A) many charged particles remained in the discharge track, and conditions for the development of a new, more powerful leader were finally created.

After bridging electrodes the development of breakdown was not finished yet, by any means, since no reverse discharge with a well conducting duct appeared for a long time. As before, cross leaders, following each other, were damped, although not completely. However, the current of every next leader was also greater than the preceding one. It was not until they reached a signigicant amount that conditions finally arise for prolonged sparking.

Thus, one can take for granted that prolonged sparking or the formation of a well conducting bridge between electrodes can start only when the leader current exceeds a certain critical value. The temperature of spark increases in this case highly enough to facilitate the mechanism of impact ionization, thermal ionization, and photo-ionization to start generating more charged particles as compared against amounts decayed during deionization, i.e. during recombination, lateral diffusion and electrode deposition.

After a certain time the current flowing through spark decreases as a result of smaller pulse amplitude and greater resistance of the discharge track. New damping of discharge starts again (see D in Fig. IV). For 170-mm long spark, current of 1 to 2.5 A proves insufficient to continue discharge without breaks.

How does breakdown develop without limitations put on discharge current, and is it to be a stepwise-leader process? Oscillograms of current I and voltage U in diagram V, Fig. 103 were recorded for a very small limiting resistance (16.6 ohms). The process of current growth up to 106 A turned out to be mono-avalanche, but without the drastic character that has been so typical of small spark gaps and stepwise leaders. From this it follows that at the beginning of the formation of breakdown electrodes were shorted-out through small-power streamer or leader, but the oroginal current was big enough to develop discharge by the mechanism of impact ionization, thermal ionization, and photo-ionization all discussed above. Breakdown was formed for about 5 microseconds. Almost the same has been fixed for the negative edge (oscillogram IV) and uniform electric field.

A peculiar effect of polarity occurs when wide gaps are broken down in distilled water. A higher voltage should be applied to the negative edge than to the positive one to break a gap with a width l, but the breakdown is formed for lower U. The delay times are much larger, however, in the case of the negative edge.

In oscillogram VI Fig. 103 one can watch at the variation of current during the pre-breakdown period at the negative edge. A slow current increas is observed during the first 120 microsecond after voltage has been applied. It is well marked only after the specified time. Based on this oscillogram in Fig. 104, curves have been constructed for the variation of voltage (1) and current (2) with time. the general picture turns out to be a little unusual. Ever-increasing current corresponds to steeply-decreasing voltage of the applied impulse. This relationship I-f(U) can be explained in terms of the formation of a powerful negative charge in water due to the capture of electrons arising during impact ionization and cold emission from the cathode. Nothing like this is observed for the breakdown of gaseous gaps.

Repeated damping of complete breakdown after its formation has also been observed in tests with other strongly-polarized liquids [243]. Oscillograms I and II, Fig. 105 were recorded for breakdown in distilled, dried-out, and filtered acetone. Discharge current was limited to 1.2 Amps. The distance between a negative steel edge and a brass plane during recording oscillogram I was equal to 3 mm. Oscillogram II was recorded for the positive edge and a plane at the distance of 3.5 mm. Undistorted amplitudes of the voltage of the pulse applied are shown by the broken line. The time before point a can be regarded as a static delay, and the further time until the steep decrease of voltage as an active delay. During the same time conditions are also created for the breakdown of polar liquid under relatively small U.

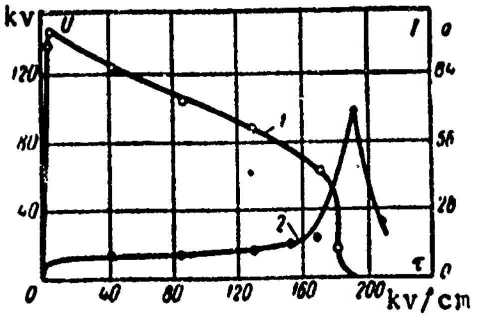


Fig. 104. Current and voltage before and during breakdown of distilled water for the negative edge and plane; 1- voltage; 2- current.

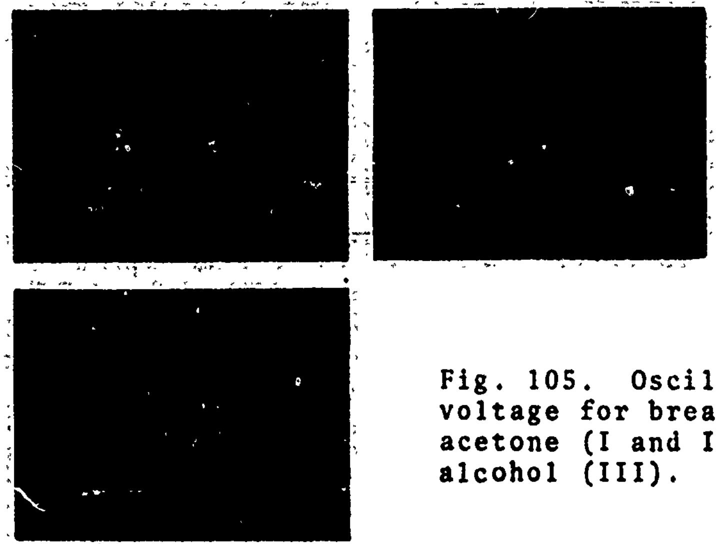


Fig. 105. Oscillograms of voltage for breakdowns in acetone (I and II) and ethyl alcohol (III).

At the first breakdown (oscillogram I) voltage decreased almost to nil, but the leader current was insufficient to continue discharge. After damping the initial leader, breakdowns were formed several times more and also were damped several times. The series-intermittent form of breakdown A (oscillogram II in Fig. 105) was recorded for the positive edge and a plane. After each of five consecutive breakdowns, the dielectric strength of the gap was restored almost completely, but after those five a subsequent large number (a series) of breakdowns was recorded for much smaller voltages.

Oscillograms III in Fig. 105 were recorded for ethyl alcohol breakdowns. For the actual limitation of discharge current, gaps with various lengths were broken down between the negative edge and a plane. The left-hand (lower) oscillogram describes the breakdown of 1.5 mm gap; the contral, 2.25 mm; and the right-hand, 2.75 mm long gap. The same irregular state has characterized the formation of breakdown. To eliminate this irregularity, discharge current should be increased a little.

It can be assumed that active radicals are formed at a certain distance from a well conducting plasma bridge under the action of ultraviolet radiation of a spark and temperature [224 and 245]. In acetone, for example, this process follows the equation

$$(CH_3)_2CO \rightarrow CH_3 - CH_3 + CH,$$

while that in ethyl alcohol corresponds to

$$C_2H_5OH \rightarrow CH_2 - CH_2 + H_2O.$$

Apart from recombination of charged particles and their electrode accumulation, deionization of spark track could have also been carried out due to combinations of the specified radicals and ionized molecules. It also seems possible that new compounds with different physico-chemical properties are formed.

On the basis fo the foregoing material one can take for granted taht limitation of discharge current is of principal importance for the mechanism of the development of breakdown. This limitation can impart the stepwise-leader character to breakdown, which is not obligatory for the unrestricted case. For breakdown of fairly long gaps between an edge and a plane in transformer oil, it was exposed that, still for limitation of discharge current by means of insulating barriers, the leader process looks like miniature lightning discharge [103 and 106].

In the case of two edges, discharge starts from both edges almost simultaneously. The leaders meet in the interelectrode gap, like in the case of lightning discharges, a leader is replaced by reverse discharge, whose existence can be guessed by bright spark flashes.

Data concerning the changes of liminescence brightness during the formation of reverse discharge and luminescence in branch nodes of long lightning sparks are presented in work [247].

CHAPTER SEVEN

SOME PROCESSES CONNECTED WITH THE BREAKDOWN OF LIQUIDS

7-1. The Length of the Breakdown Process

From the curves presented in Figures 41 and 43 it was evident that the E_{br} of liquid hydrocarbons increases when short rectangular pulses affect the spark gaps several tens of microns in length. It is obvious that the statistical delay and formation of breakdown at a given E_{br} took a quite definite time. Some data concerning this delay were presented in section 6-2.

Experiments with N-hexane showed that with a length of the spark gap $L = 5 \times 10^{-3}$ cm the time of statistical delay weakly depends on the voltage of the applied field in a range of from 1.7 to 1.9 millivolts/cm. With $E \doteq 1.7$, 1.8, and 1.9 millivolts/cm it proved to be equal to from 0.3 to 0.7, from 0.3 to 2.0, and from 0.3 to 0.5 microseconds respectively. Apparently, for the indicated gap the minimum time of delay is approximately equal to 0.4 microseconds (L.233 and 234). It is comparatively small during rough preparation of the ball cathode made of stainless steel even with a field intensity of 1.4 millivolts/cm (from 0.3 to 2.3 microseconds). Polishing of the cathode while the other conditions remain unchanged increases this time.

The following conclusion results from what has been set forth: an increase of the E_{br} of liquid hydrocarbons is basically caused by the fact that the length of the rectangular pulses was commensurate with or even less than the time of statistical delay. But what is the case with longer gaps? As of yet this question has not been studied in detail, but, for example, according to the oscillagrams of IV of Figure 97, it is possible to conclude that, with L = 150 mm and with electrodes made with a point and a plane, the minimum time of delay of the breakdown of distilled water is equal to around 5 microseconds.

As of yet it is impossible to say anything about those values of E at which it will decrease, but, if this did not happen, then it would be possible only with very large values of E to breach the indicated gap. The formation mechanism of the breakdown would then be quite different.

What time does the formation of the breakdown itself take, and on what does it depend? In the literature there are indications that the progressive development of the breakdown which has begun can end even in a time of 10^{-9} seconds (L. 111). According to other data, this time is several orders larger both for liquid and for solid dielectrics (L.248). For example, in (L.65, 249-252) hypotheses were expressed concerning the probable length of the breakdown of from 10^{-6} to 10^{-8} seconds. In some cases in order to be persuasive they refer to the formation of breakdown of gas gaps, paying no attention to the special properties of the state of aggregation, the length of the spark gap, and so forth.

The length of the breakdown process in transformer and castor oils was determined according to the plan in Figure 106 (L.252). High-frequency oscillations with a period $\tau_1 = 9 \times 10^{-9}$seconds were superimposed on the time base A of a high-voltage cathode oscillograph KO. It is known that the deflecting plates of the cathode oscillograph A and B are situated perpendicular to each other, and the form of the pulse wave during normal operation is recorded as it is presented in B and α of Figure 106. Graduation by time γ is usually applied from an outside high-frequency generator. In Figure 106, the same form of the pulse wave is shown in β as in α, only with the imposition of high-frequency oscillations on the voltage of the time plates of A. The period can be determined according to the time τ_1, and the length of the breakdown according to τ_2.

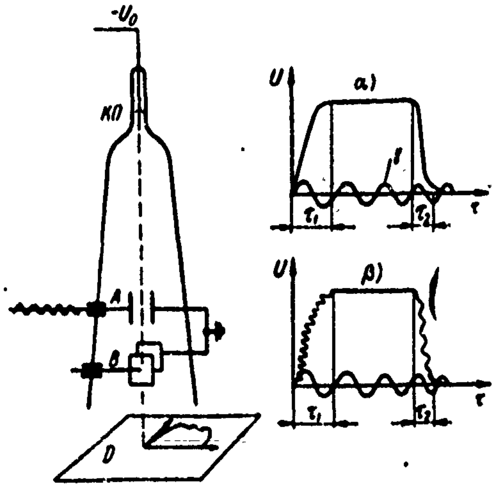


Fig. 106. A plan for recording the length of the breakdown process of liquid dielectrics by a cathode oscillograph.

Transformer and castor oils were studied in the experiments, as well as distilled water. The recorded oscillograms of breakdown are presented in Figure 107. Some explanations of them are given in Table 43.

The oscillogram A in Figure 107, I was recorded during the first breakdown,,and B during the second breakdown of one and the same portion of transformer oil. The electron beam of the cathode oscillograph was not focused sufficiently well, and for this reason it was difficult to observe the appearance of low-power streamers during the time of statiscal delay, but traces of them are visible on the crest of the pulse of oscillogram II.

The 2.5 cm gap between electrodes in distilled water was breached during a field intensity that was greater than the lowest E_{br}. When recording Δ_1 the breakdown occured at a greater delay. It is not visible on photograph III (behind the screen).

In Figure 107, IV two different oscillograms have been taken down: a_2, during the breakdown of transformer oil; and b_2, during spark over along the surface of the insulator (see Table 43). The period of the sinusoidal oscillations graduated by time on the axes of the abcissas of all oscillograms is equal to 5×10^{-7} seconds.

Table 43. Explanations of the Oscillograms in Fig. 107.

Oscillogram	Liquids	Form of Electrodes	Distance between electrodes mm	Breakdown voltage kV	Decay of breakdown μsec
I	transformer oil	negative	80	159&178	47 & 42
II	castor oil	positive edge and plane	120	183	3
III	distilled water	spheres d = 62.5 mm	25	170	21
IV a	transformer oil	positive edge and plane	60	200	15
IV b	bracket insulator of porcelain with metallic bushings	bushings of bracket insulator	250	221	8

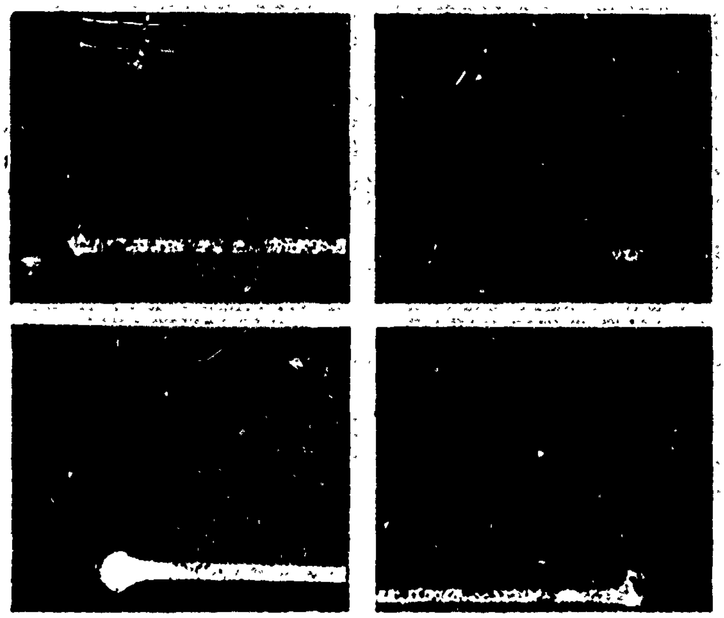


Fig. 107. Oscillograms of the Breakdown and Sparkover of Various Dielectrics.

In experiments with transformer oil the influence of the form of the electrodes, distance between them, and the size of the voltage with a constant l on the length of the breakdown was studied. Curves of the voltage reduction during the formation of the breakdown of transformer oil were constructed according to the oscillograms which were recorded (Fig. 108). This lowering in percentages has been plotted along the axis of the ordinate. That pulse amplitude at which a noticeable reduction of voltage occured that is, at which formation of breakdown began, was taken as 100 percent. This point on one of the oscillograms of Figure 107, is designated by the letter a. Curve 1 in Figure 108 was constructed according to the data of the indicated oscillogram.

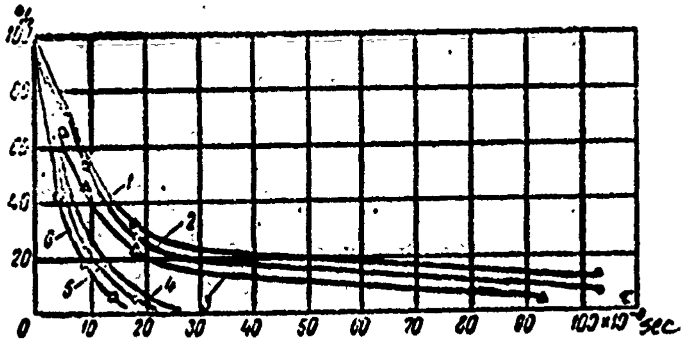


Fig. 108. The curves of voltage reduction during the formation of the breakdown of well-cleaned transformer oil.

The remaining oscillograms, according to which curves 2 through 6 were constructed, are not presented here. Even the time of the beginning of the discharge was reckoned from point a. The numerical data for Figure 108 are presented in Table 44. Identical gaps of l = 5 and 50 millimeters were breached with different U_{br}.

From Figure 108 and Table 44 it follows that the length of the discharge is shortened with a decrease of l (see curves 1 and 2); the same occurs even in the case of increasing the voltage while l remains constant (see Curves 2 and 3, as well as 5 and 6). With breakdowns of comparatively long spark gaps between point and plane in a time of 2×10^{-7} seconds the voltage is decreased by from 70 to 80 percent. After this, the speed of reduction sharply decreases.

The curves of Figure 109 were constructed according to the oscillograms of II through IV of Figure 107. The smalllest length was fixed during the breakdown of distilled water (a gap of 2.5 cm). During the breakdown of castor oil and the spark over along the surface of the insulator, the process takes place with delay at the first moment. This delay is stretched to approximately 1.5 microseconds during the spark over of the insulator.

The mechanisms of voltage reduction during the breakdown of transformer oil and air are different for a positive point and plane. This reduction also occurs with some delay in the beginning of the formation of the breakdown of the air interval (L.253); such a delay is not observed in the case of the case of the transformer oil.

The formation of low-power streamers is possible in the pre-disruption time; without limiting the discharge current, they cause barely noticeable voltage reductions (see section 6-2). Such a streamer can even short-circuit the electrodes, but, if it is quickly suppressed, then it is possible not to notice the actually occurring breakdown without oscillograph recording. In this case it is possible not to hear the shattering sound which usually accompanies the breakdown.

From oscillogram IV of Figure 103 it was apparent that

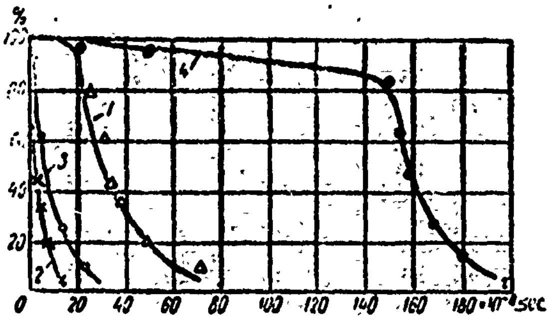


Fig. 109. Curves of the voltage reduction during the formation of the breakdowns of liquids and the spark over along the surface of the porcelain insulator.

1-castor oil (oscillogram II of Fig. 107); 2-distilled water (oscillogram III of Fig. 107); 3-transformer oil (oscillogram a2 of IV of Fig. 107); 4-during the formation of the spark over along a bracket insulator made of porcelain

that the individual leaders in the water which short circuit the gap l = 17 cm between the positive point and plane are formed very quickly. The speed of the positive leaders in water is equal approximately 1.6 x 10^6 cm/sec (L.104), while in the transformer oil for gaps of from 30 to 50 cm it is equal to from 1 to 5.3 x 10^7 cm/sec (L.254). Negative leaders in the same transformer oil spread with a somewhat lower speed (from 3.3 to 8.3 x 10^6 cm/sec).

At such speeds there may really be required approximately 10^{-9} seconds for the short

Table 44. Explanation of Fig. 108.

No. of curves	Shape of electrodes	Distance between electrodes, mm	Breakdown voltage, kV	Time of statistical lag of breakdown, μsec
1	Negative edge and plane	80.0	178	47.0
2	Same	50.0	132	28.0
3	Same	50.0	169	15.0
4	Same	30.0	200	1.5
5	Spheres d = 62.5 mm	5.0	184	5.0
6	Same	5.0	208	1.5

circuiting by the positive leader of a gap of, for example, 0.01 cm. In the case of turning on very limiting resistors during the breakdown, the capacitance of the electrodes does not have time to recharge, even if a comparatively low-power leader is formed. The voltage on the electrodes will then drop sharply, that is, a breakdown will occur. And such leaders are formed very quickly (see oscillogram IV of Fig. 103); but, without limiting resistors, such a leader causes a barely noticeable voltage reduction. But the breakdown occurs only after the formation of a good conducting bridge, and for this reason a considerable time is required. According to oscillogram V of Fig. 103, approximately 5 microseconds was required to complete the breakdown of the gap with $l = 17$ cm. Moreover, at a given l this time depends on the size of the excess voltage on the spark gap (see Fig. 108), as well as on the chemical composition and structure of the liquid dielectric.

Thus, much depends on the conditions of the experiment. Those reseachers who stated that the length of the breakdown is equal to 10^{-8} seconds or even less might not have made a mistake. In exactly the same way there are no grounds to suspect error on the part of those who indicated a time of 10^{-6} seconds.

One must pay attention to the features of the structure of the liquids in connection with the capture of free electrons. The existence of a small group molecules with a relatively high degree of ordering has already been mentioned (see section 1-2). Such groups evidently consist of several tens of molecules (L. 255).

It is known from wave mechanics that at each defect of a regular lattice, even including the vicinity near the surface of the crystal, the moduli of the wave functions have clearly expressed maxima (L.256 and 257). This must indicate that the limiting surfaces of the crystals may be carriers of the mass centers of electron capture. Evidently, these ideas can even be transferred to crystal-like groups of liquids (L.89). If this is so, then even the structure of crystal-like groups of liquid dielectrics must exert a noticeable influence on the length of the breakdown.

According to the curves of Fig. 108, even the currents which flow through the discharge channel during breakdown can be determined depending on the time. The methodology of the approximate calculation of the currents for solid and gaseous dielectrics was presented in (L.239 and 258). It can evidently be used even for liquids.

7-2. Post-breakdown Processes

Usually, during breakdown of dielectrics without limitation of the discharge, a good conducting bridge between the electrons is formed and the voltage sharply drops, almost to zero. No matter what the chemical composition of the liquid, one and the same effect is obtained. But the experiments showed that, if it is necessary to limit the discharge current, the voltage change during the burning of the spark after the initial breakdown will be determined by the specific features of the liquid dielectric.

Such experiments were carried out according to the plan of Figure 95b (L.259 and 260). The liquids were cleaned by chemical means, distilled, dried, and filtered. At a temperature of around 20 C one and the same gap (0.2 mm) between polished balls 11 mm in diameter made of stainless steel was always breached. The breakdown of one and the same liquid was produced with different limiting resistances R_0 (see Fig. 95) ranging from zero to several meg ohms. The resistance R_0

plus R was equal to 8×10^4 ohms. At the given R_0 one portion of the liquid with a capacity of approximately 0.3 liters was breached.

After changing the sample the electrodes were carefully polished, washed, and dried at a temperature of 200 C under a vacuum. Recording of the charges was produced by a cathode oscillograph. Besides the recording of the voltages during the burning of the spark, in some cases even the currents flowing through the discharge channel were recorded. Non-polar, weakly polar, and strongly polar liquids were studied.

Table 45. Explanation of Oscillogram in Figure 110.

Oscillogram number	Limiting resistance, ohms	Initial breakdown voltage, kV	Time (τ) of voltage peaks (μsec) and their amplitudes U (kV)						Curent I_3, a
			1st peak		2nd peak		3rd peak		
			τ	U	τ	U	τ	U	
I	0	16,0	250	8,8	—	—	770	0,7	1,23
II	10^5	16,5	230	6,4	430	3,5	657	3,8	0,144
III	$5 \cdot 10^5$	15,3	230	3,8	400	4,2	555	3,4	$2{,}9 \cdot 10^{-2}$
IV	10^6	14,4	220	4,3	360	3,6	508	3,6	$1{,}35 \cdot 10^{-2}$
V	$2 \cdot 10^6$	15,0	200	3,0	304	2,9	355	2,4	$7 \cdot 10^{-3}$
VI	$3 \cdot 10^6$	10,8	170	2,0	290	3,3	450	2,4	$3{,}45 \cdot 10^{-3}$

Oscillograms of the breakdown of xylene are presented in Figure 110. Technical xylene was studied without isolation of the isomers. Light fractions with a boiling point lower than 129 C were removed during fractionation. The numerical material relating to these oscillograms is presented in Table 45.

It is evident from Oscillogram I that within approximately 250 microseconds there arose a sharp and quite intense de-ionization of the discharge channel. The voltage on the spark gap

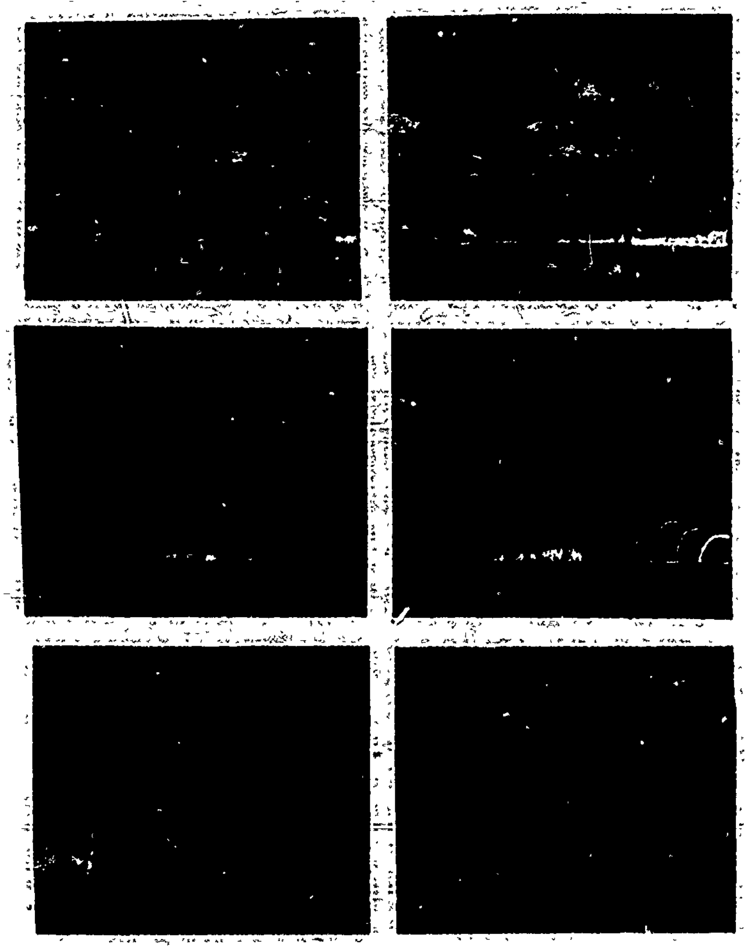


Fig. 110. Oscillograms of the breakdown of xylene with various limitations of the discharge current.

during this increased to 8.8 kv. Further growth proves to be impossible because a repeated breakdown was formed. Consequently, the E_{br} of the strongly ionized spark gap decreased by almost two times. The reason for the de-ionization of the discharge channel might have been the ejection of liquid as a result of increasing the pressure in the gas medium during the burning of the spark.

It may be assumed that ejections of this type occurred only after a certain length of time, in the course of which properties of the plastic deformation of the xylene were able to appear. There is no doubt that after de-ionization in the discharge chamber there still remained many free electrons, which even facillated the formation of the subsequent breakdown at a voltage that was almost two times lower. Another reason for the sharp de-ionization of the discharge channel might have been the lowering of the temperature of the spark to the value at which, after disintegration of the complex molecules the process of association began, accompanied by the recombination of charged particles and the sharp fall of the intensity of the thermo- and photo-ionization.

Oscillogram II of Figure 110 was recorded with R_0 equal to 10^5 ohms. In comparison with the preceeding recording, the discharged current decreased by several times. There is no doubt that the temperature of the spark at this time decreased, and the radius of the channel shortened. Two more peaks have been fixed on this oscillogram, after approximately 430 and 667 microseconds. If the abrupt de-ionization occurred as a result of the ejection of the liquid, then the pressure within the discharge channel decreased when the temperature of the spark was lowered, and the ejection turned out to less intensive. For this reason, even more charged particles remained in the space, and a repeated breakdown was able to form at an even lower voltage (6.4 kv).

There arises the question of why three voltage peaks appeared when the discharged current was reduced, that is, why did a triple jump-shaped de-ionization of the discharge channel take place, while with an even greater limitation of such currents there appeared an already complete series of peaks (oscillograms III through 6). It may be assumed that during the one charge the de-ionization was able to occur both from the ejection of liquids and from the cooling of the spark channel. In this case, when the discharged current is large, and, consequently, the pressure in the channel is great, the appearance of the ejection of liquid is probable. But with small currents the jump-shaped de-ionization was even able to occur as a result of the cooling of the channel to a certain critical temperature T_k. According to the oscillograms of the breakdown of certain other insulating liquids it was possible to conclude that the reason for the jump-shaped de-ionization must be looked for mainly in the abrupt cooling of the spark.

From all the oscillograms of Figure 110 it is evident that a series of discharges at small amplitudes is observed immediately after the initial breakdown and the many subsequent breakdowns. Attention must be paid to the fact that a certain amount of electricity $Q = CU_{br}$ was stored in the capacitants of the interelectrode gap and feed C before the breakdown. This Q was discharged across the spark during the formation of the breakdown. Additional thermal energy was released from the flowing of the current $I = dQ/d\tau$ in the channel of the spark, and, consequently, the temperature of the spark also rose for a certain small length of time.

The size of this current can be determined from the solution of the differential equations for the substitution plan in Figure 111. At the instant when $\tau = 0$ an impulse of the form

$$U = E_0(e^{-\alpha\tau} - e^{-\beta\tau}). \qquad (41)$$

is switched in by closing the key K_1 from the impulse generator (U_0).

At a certain moment τ_0, when the capitance is charged to U_{br}, the key K_2 is switched on, that is, the breakdown of the liquid occurs. At the same time, the capacitance C is shunted by the resistance of the discharge channel r_2, which is assumed to be unchanging.

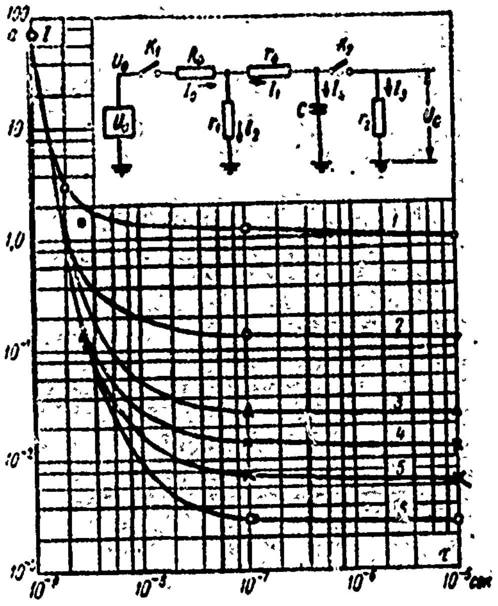


Fig. 111. The substition plan in the breakdown of liquids, and curves of the currents depending on the time in the breakdowns of xylene.

1 — $r_0 = 0$; 2 — $r_0 = 10^3$ ом; 3 — $r_0 = 5\cdot10^3$ ом; 4 — $r_0 = 10^4$ ом; 5 — $r_0 = 2\cdot10^4$ ом; 6 — $r_0 = 3\cdot10^4$ ом

We will determine the current flowing through the spark in a function of time. The equations for the instant

$$0 \le \tau \le \tau_0$$

when only the key K_1 has been closed (before the breakdown), will be the following:

$$\left.\begin{aligned} &U_0 = I_0 R_0 + I_2 r; \quad I_2 r = I_1 r_0 + U_c; \\ &I_0 = I_1 + I_2; \quad U_c = \frac{1}{C}\int_0^{\tau} I_1 d\tau. \end{aligned}\right\} \tag{42}$$

After the Laplace transforms $\bar{f} = \int_0^\infty f(\tau) e^{-p\tau} d\tau$, these equations can be represenred in working form:

$$\left.\begin{aligned} &E_0\left(\frac{1}{p+\alpha} - \frac{1}{p+\beta}\right) = \bar{I}_0 R_0 + \bar{I}_2 r; \\ &\bar{I}_2 r = \bar{I}_1 r + \bar{U}_c; \quad \bar{I}_0 = \bar{I}_1 + \bar{I}_2; \quad \bar{U}_c = \frac{\bar{I}_1}{Cp}. \end{aligned}\right| \tag{43}$$

excluding streamers:

$$\bar{U}_c = \frac{E_0 r(\beta-\alpha)}{(p+\alpha)(p+\beta)\left[Cp(R_0 r + R_0 r_0 + r r_0) + R_0 + r\right]}. \tag{44}$$

The specific points for simple deductions are equal:

$$p_1 = -\alpha; \quad p_2 = -\beta; \quad p_3 = -\frac{R_0 + r}{C(R_0 r + R_0 r_0 + r r_0)} = -\gamma; \quad U_c(\tau) = \frac{1}{2\pi i}\int_L \bar{U}_c(p) e^{p\tau} dp = \sum_{k=1}^{n} (a_{-1})_{p=p_k} =$$

$$= \frac{E_0 r \gamma}{R_0 + r}\left[\frac{e^{-\alpha\tau}}{\gamma-\alpha} - \frac{e^{-\beta\tau}}{\gamma-\beta} + \frac{(\beta-\alpha)e^{-\gamma\tau}}{(\gamma-\alpha)(\gamma-\beta)}\right]. \tag{45}$$

For the interval $\tau_0 \le \tau \le \infty$, when the key K_2 is closed, the system of equations in working form will be the following:

$$\left.\begin{aligned} &\bar{I}_0 R_0 + \bar{I}_2 r = E_0\left(\frac{e^{-\alpha\tau_0}}{p+\alpha} - \frac{e^{-\beta\tau_0}}{p+\beta}\right); \\ &\bar{I}_2 r = \bar{I}_1 r_0 + \bar{U}_c; \quad \bar{I}_0 = \bar{I}_1 + \bar{I}_2; \\ &\bar{I}_1 = \bar{I}_3 + \bar{I}_4; \quad \bar{U}_c = \bar{I}_3 r_2; \\ &\bar{U}_c = \int_0^\infty \left(U'_{c|\tau=\tau_0} + \frac{1}{C}\int_0^{\tau'} I_4 d\tau'\right) e^{-p\tau'} d\tau' = \frac{U'_{c|\tau=\tau_0}}{p} + \frac{\bar{I}_4}{Cp}; \end{aligned}\right| \tag{46}$$

here $\tau' = \tau - \tau_0$, while $U'_c/_{\tau=\tau_0}$ is determined from (45) by replacing τ for τ_0.

From the system of equations of (46), excluding I_0, I_1, I_2, I_3, and I_4, we will determine

$$\bar{U}_c = \frac{E_0\gamma r}{R_0+r}\left[\frac{(p+\beta)e^{-\alpha\tau_0}-(p+\alpha)e^{-\beta\tau_0}}{(p+\alpha)(p+\beta)(p+\delta)} - \frac{U'_c}{p+\delta}\right],$$

where

$$\delta = \frac{R_0 r + R_0 r_0 + r r_0 + R_0 r_2 + r r_2}{C r_2 (R_0 r + R_0 r_0 + r r_0)}.$$

With specific points $p_1 = -\alpha$; $p_2 = -\beta$ and $p_2 = -\delta$ we will get:

$$U_c(\tau) = \frac{E_0\gamma r}{R_0+r}\left\{\frac{e^{-\alpha\tau}}{\delta-\alpha} - \frac{e^{-\beta\tau}}{\delta-\beta} + \left[\frac{(\delta-\alpha)e^{-\beta\tau_0}-(\delta-\beta)e^{-\alpha\tau_0}}{(\delta-\alpha)(\delta-\beta)}\right]e^{-\delta(\tau-\tau_0)} + U'_c e^{-\delta(\tau-\tau_0)}\right\}. \quad (47)$$

In this formula, according to (45),

$$U'_c = \frac{e^{-\alpha\tau_0}}{\gamma-\alpha} - \frac{e^{-\beta\tau_0}}{\gamma-\beta} + \frac{(\beta-\alpha)e^{-\gamma\tau_0}}{(\gamma-\alpha)(\gamma-\beta)}.$$

for the current I_2, which flows through the spark channel, we may write:

$$I_2 = \frac{U_c(\tau)}{r_2}. \quad (48)$$

The form of the wave U_0 and its parameters can be approximately determined from the oscillograms for U_c, for example, oscillogram V of Figure 110. Several impulses have been recorded here without breakdown, that is, only with the closing of key K_1 (Fig. 111).

From the system of equations (42) we get:

$$U_0 = A\frac{dU_c}{d\tau} + BU_c; \quad I_1 = C\frac{dU_c}{d\tau}, \quad (49)$$

where $$A = \frac{C(R_0 r + R_0 r_0 + r r_0)}{r}; \quad B = \frac{R_0+r}{r}.$$

The form of the impulse according to oscillogram V of

Figure 110, can also be nicely represented as the difference of two exponential, functions:

$$U_c = U_1(e^{-\xi\tau} - e^{-\chi\tau}).$$

It is easy to determine from the indicatee oscillogram the time τ_{maximum}, during which the amplitude reached its greatest value, and the time τ_p, during which it falls to its half value. With τ_{maximum} and τ_p known, it is possible to determine U_1, ξ and χ according to the diagram (L.261).

After substituting the deritative $\frac{dU_c}{d\tau}$ in (49), the expression for U_0 will get the following form:

$$U_0 = U_1[(B - \xi A)e^{-\xi\tau} - (B - \chi A)e^{-\chi\tau}]. \tag{50}$$

From (50), with $\frac{dU_0}{d\tau}$, the value of τ'_{maximum} will be equal to:

$$\tau'_{\text{макс}} = \frac{1}{\chi - \xi}\ln\frac{(B - \chi A)\chi}{(B - \xi A)\xi},$$

while the time of the half decrease of the greatest amplitude τ'_p can be found from graphically constructing the impulse according to (50). With τ'_{maximum} and τ'_p known, the constants E_0, α and β in (41) and (47) are also determined according to (L.261).

The curves of $I_3 = f(\tau)$ in Figure 111 were constructed for xylene according to the formula of (48) with r_2 equal to 10 ohms and the parameters of plan 111 known. The current I_3 consists of two components: 1) the quickly falling I'_3 from discharge of the capacitance C and 2) the I''_3 from the applied voltage U_0, which is established after 4 x 10^{-8} seconds. The computed values of I''_3 are even presented in the last graph of Table 45. It follows from the curves of Figure 111 that the current I'_3 can exceed I''_3 by several orders. The influence of this rapidl falling current should show up only in very small segments of time after completion of the breakdowns.

It has already been noted that, after the initial breakdown and certain subsequent ones, multiple discharges at amplitudes at of from 0.6 to 0.8 kv, that is, from 30 to 40 kv/cm, take place. It is well known that breakdowns of not too small air gaps under normal conditions occur with approximately the same intensities. The latter circumstance provides certain bases for assuming that the discharges occur in a gas atmosphere, although with high pressure, still strongly ionized. It is necessary to consume a certain energy in order to create such an atmosphere. For this reason, with large values of r_0, when the constituent of the current I_3'' is small, the creation of a gas atmosphere in the area of the discharge channel can occur due to the I_3' component.

The same oscillograms of the breakdown of castor oil and air gap 0.2 mm in length)L.262) are presented for comparison in Figure LL2. The explanatory numerical data for these oscillograms is located in Table 46.

Table 46. Explanation of oscillogram in Figure 112.

Dielectric	Oscillogram no.	Limiting resistance, ohms	Initial breakdown voltage kV	Voltage of subsequent breakdowns kV	Voltage at which discharge is attenuated, kV	Discharge attenuation time μsec	Current I_3, a
castor oil	I	0	12.30	0.2-0.4	-	-	1.1
	II	10^5	12.20	0.2-0.7	-	-	0.1
	III	10^6	12.00	0.7-3.0	-	-	10^{-2}
air, normal conditions	IV	$2 \cdot 10^6$	10.70	0.7-5.3	4.6	378	$4 \cdot 10^{-3}$
	V	10^5	1.17	0.52-1.0	0.9	200	$1.4 \cdot 10^{-2}$
	VI	$2 \cdot 10^6$	1.27	-	1.0	0	$7\ 10^{-4}$

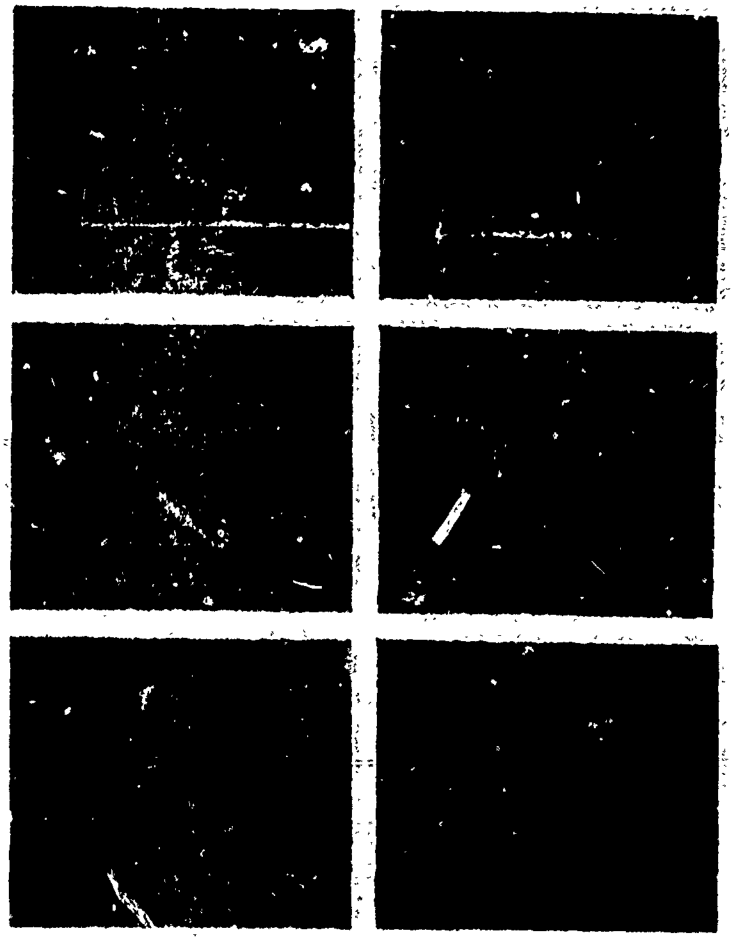


Fig. 112. Oscillograms of the breakdown of castor oil (I - IV) and of air (V and VI) with different limitations of the discharge current.

On the first two oscillograms of Figure 112 only discharges with low intensities are fixed after the initial breakdown. There also does not occur a sharp de-ionization in the castor oil with a limiting resistance of r_0 equal to 10^5 ohms. It becomes noticeable only with r_0 equal to 10^6 ohms. Just as with breakdowns of xylene after each such de-ionization the voltage on the electrodes of the gap in question increased, and a new breakdown formed. Evidently, the intensity of the thermal and photo ionizations in the castor oil was great with r_0 less than 10^6 ohms, and the production of charged particles predominated over their decrease. Discharges at low field intensities (around 30 kv/cm) probable also occurred in the gas atmosphere of the discharge channel.

With r_0 equal to 2×10^6 ohms, the temperature of the spark, evidently, was not so high, and the de-ionized processes were not so intense. In oscillogram IV the small fall of voltage on the crest of one of the peaks (see A), calls attention to itself. The progressive development of the already-begun breakdown was here suppressed by de-ionized processes even with the comparatively ionization of the discharge channel.

Post breakdown discharges in the air at certain values of r_0 take place intermittently, as well, but the dynamics of the discharge has many distinctive features.

It is evident from a comparison of the oscillograms recorded with identical values of r_0 in Figures 110 and 112 that the post breakdown processes in xylene are strongly differentiated from the same processes in castor oil and air. This difference is obviously caused by the properties of the physical-chemical nature of the liquids and air.

One more series of such oscillograms of the breakdown of pentachlordiphenyl (chlorinated diphenyl) is presented in Figure 113. The explanations for these oscillograms are assembled in Table 47.

Table 47. Explanation of oscillogram in Fig. 113.

Oscillogram no.	Limiting resistance	Initial breakdown voltage	Time of beginning of discharges, μsec	Amplitude for beginning of discharges, kV	Amplitude of discharges 1060 μsec from beginning of pulse supply, kV
I	0	15.0	670	0.29	0.8
II	10^5	14.0	200	0.46	1.2
III	10^6	14.5	40	0.60	1.0
IV	$2 \cdot 10^6$	15.2	60	0.50	1.1
V	$3 \cdot 10^6$	13.5	40	0.50	1.1
VI	$7 \cdot 10^6$	10.5	344	1.70	1.7

Chlorinated diphenyl, as is known, possesses great viscosity. Quite probably, it is due to exactly this situation that not one sharp and significant voltage peak was fixed after the initial breakdown. The discharges occurred only at low intensities (from 40 to 85 kv/cm) and also, apparently, in a gas atmosphere of the channel. The pressure in it was evidently not large enough to overcome the molecular forces of cohesion. For this reason, the ejection of liquid form the inter-electrode space could not develop. It is also possible that in the process of association with the lowering of temperature there were formed not original molecules, but more stable, gaseous ones, and that the gas atmosphere was preserved until the end of the discharge.

Oscillogram VI of Figure 113 was recorded after feeding to the gap in question a very large number of impulses with amplitudes consierably less than breakdown ones. These impulses of preliminary ionization prepared a breakdown with a lower intensity of the applied electrical field (approx. 0.52 mmv/cm). A repeated breakdown was not able to form after completion of the initial breakdown in the time of approximately 330 microseconds (see A). The general picture of the discharges also turned out to be different from the preceding ones.

During the oscillographing of the post breakdown processes it was observed that the individual properties of the liquids appear most clearly with limiting resistances of r_0 equal to 10^6 ohms. Comparatively large currents flow through the spark in the case of lower values of r_0. In this case, the temperature of the discharge channel is high; the thermal and photo ionization are intense; and conditions favorable to the predominance of de-ionized processes either do not appear for a long time or do not appear at all.

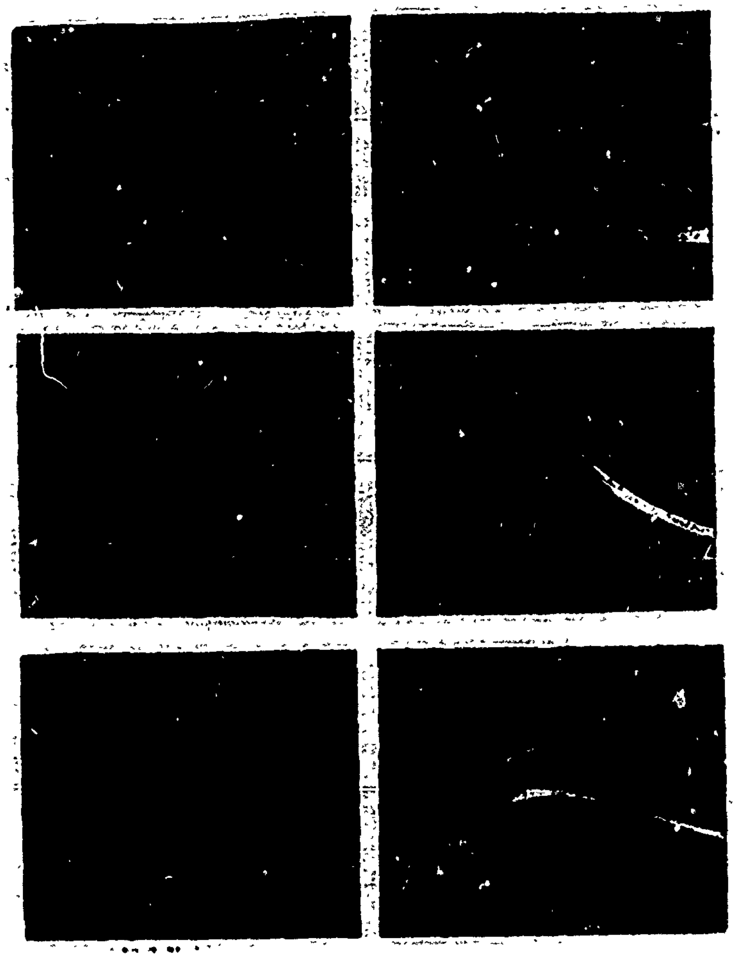


Fig. 113. Oscillograms of the breakdown of pentachloradiphenyl (chlorinated byphenol) with different limitations of the discharge current.

The individual properties of the liquids are not noticeably manifested even with two great values of r_0 because the temperature of the spark is low and the deionized processes are quite intense. Re-establishment of the dielectric strength of the gap in question occurred quite quickly, and the discharge soon breaks off. Subsequently breakdowns with slow charging of the capacitance C rarely occur, and it is difficult to discover the characteristic features of the discharge.

The oscillograms in Figure 114 were recorded at exactly the most favorable limiting resistance r_0 = 0.85 and 1 x 10^6 ohms (= 0.2 mm). Explanations of these oscillograms are presented in Table 48.

Table 48

Explanations of Oscillograms in Figure 114

Oscillogram number	Liquid	Breakdown voltage, kV
I	3% solution ethylcellulose in toluol	11.0
II	Aniline (light)	14.5
III	Oxidized aniline (dark)	10.0
IV	Silico-organic liquid (calorie-2)	10.0
V	Toluol	11.5
VI	Carbon tetrachloride	14.0

Pure analene was obtained from supply organizations in a special vessel, and it did not undergo refining. Oxidized analene was obtained from light analene by means of oxidizing it in the air.

On oscillogram I of Figure 114, the section 10 is characteristic. The voltage, which was equal to 3 kv, for nearly 300 microseconds almost did not change. The discharge channel was in a state of high ionization, and the formation of the next breakdown was delayed. During this time a dynamic equilibrium, as it were, was established, in which the falling count of the impulse flowed along the ever-increasing resistance of the discharge channel. After 300 microseconds the gap was breached with E approximately equal to 150 kv/cm.

There occurred a rather abrupt and almost complete de-ionization of the discharge channel (see peak k of oscillogram II) with the analene (C_6H_7N) after approximately 280 microseconds, evidently also from the ejection of liquid, but after a short period of time a new breakdown formed.

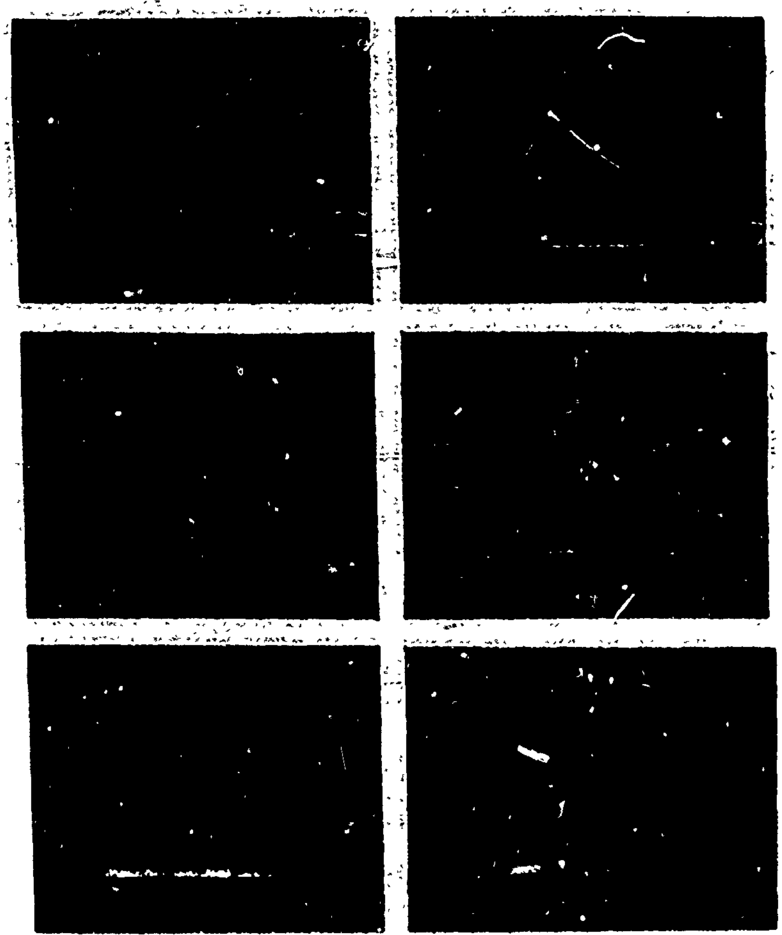


Fig. 114. Oscillograms of the breakdown of different liquids with limiting distances of r_0 equal to 0.85 and 1×10^6 ohms.

Sections 1 and 2 on oscillogram II are characteristic. They formed at a considerable lower voltage, in contrast to the conditions of n of oscillogram I. They weren't observed at all with dark (oxidized) analene (see Oscillogram III). However, the conditions of N existed a comparatively long time after the four subsequent breakdowns. This circumstance testifies to the fact that the molecules of the oxidized analene are less thermally stable than are the molecules of light analene.

The appearance of the conditions of N can also be ovbserved after each subsequent breakdown with the silicon-organic liquid (calorie 2). It follows from this that the intensity of the formation of the gas atmosphere during the thermal decomposition of complex molecules is quite significant in the silicon-organic liquid. After the initial, second, third, and fourth breakdowns, the conditions of N existed for 170, 100, 82, and 46 microseconds respectively. To the extent that the temperature of the spark was lowered, the intensity of the thermal decomposition of the molecules, naturally, was lowered, and, consequently, the duration of the existence of the gas atmosphere inside the discharge channel also decreased.

The breakdown of toluene occurred after a double application of impulses with a maximum amplitutude of 16 kv (0.8 mv/cm). And the breakdown voltage (11.5 kv) proved to be considerably less.

It has already been mentioned above, that when a voltage close to the breakdown voltage is switched on during the breakdown delay, formation of electron avalanches and electron capture by the molecules of the liquid take place. Consequently, a space charge forms in the inter-electrode gap.

Inasmuch as the volume increases when a solid body melts, it is assumed that there is a large number of micro cavities (cavitation spaces) in liquids and that they appear in random places and quickly disappear. When a space charge exists the probability of formation of such micro cavities as a result of electrostatic repulstion should increase. The electrons falling into such places can acquire an energy which is sufficient for ionization even at voltages that are lower than breakdown ones. The above-mentioned circumstance apparently serves as one of the reasons for the lowering of values of U_{br} when an impulse voltage with maximum amplitude somewhat less than U_{br} is repeatedly switched to the electrodes of the gap in question. Certain structural properties of toluene appear in this. The influence of such properties can be illustrated based on the example of liquified gases. The breakdown intensity of liquid helium, for example, comprises only 0.7 mv/cm, while that of liquid nitrogen comprises 1.6 mv/cm (L.263).

In strongly ionized toluene, the subsequent breakdowns form at comparatively low intensities (from 0.12 to 0.13 mv/cm) for possibly the same reason. Because of this circumstance, the picture of the post breakdown discharge turns out to be somewhat unusual.

Discharges after the initial breakdown in carbon tetra choride usually stop early (see Oscillogram VI of Fig. 114), even with comparatively large field intensities (0.225 mv/cm). This can be explained by the fact that the de-ionized processes in carbon tetra chloride are quite intense. On Oscillogram VI it is possible to follow the degeneration of charges of Type N at low intensities (see b) in special conditions which are analogous to n of Oscillogram I as well as 1 and 2 of Oscillogram II. In accordance with the definite growth of the resistance of the discharge channel and the similar decrease of the impulse current, during which the voltage remains almost constant for a long time, these conditions may be called balanced. The post-breakdown processes in distilled water proceed completely differently (L.264). One can get an idea of them from the current oscillograms I through III of Figure 115. They were recorded during breakdowns of a gap also equal to 0.2 mm and with r_0 equal to 0. The period of the sinusoidal oscillations graduated by time on the axes of the abcissas of these oscillograms comprises 2.5 microseconds. The almost horizontal sections of 1, 2, 3, and 4 on the oscillograms of I represent currents of conductivity during the delay of the breakdown. Oscillogram IV of Illustration I of Figure 115 was recorded with E_{br} equal to 100 kv/cm, while the others were recorded with a gradual reduction of E to the minimum breakdown value.

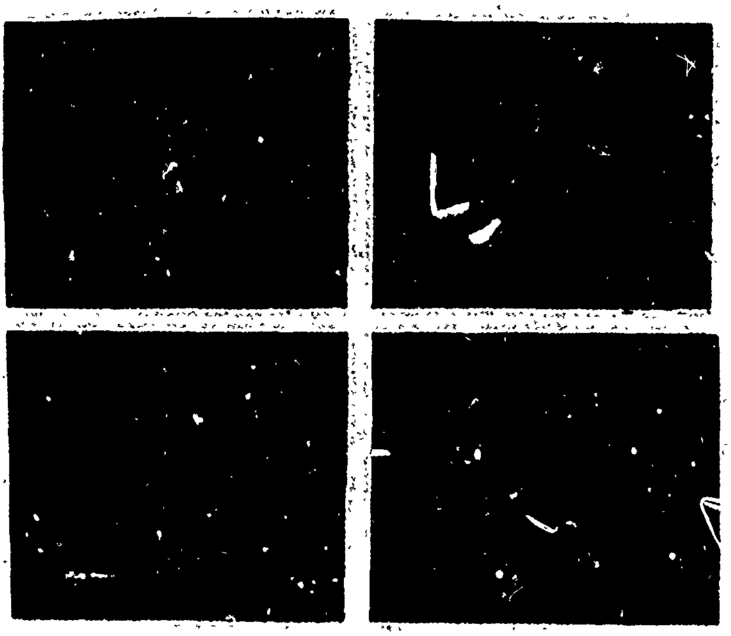


Fig. 115. Oscillograms of the currents during the breakdowns of distilled water and silicon-organic liquid (IV).
I-the electrodes are steel balls;II-are negative steel points and a brass plane;III-2 steel points;IV-steel balls

The development of breakdown occurs intermittently as well without very large excess voltages in the gap in question between the balls (a_1-a_4).

A comparatively strong streamer a_1, which had formed at the maximum voltage, was suppressed by de-ionized processes. The progressive development of the breakdowns stopped, but after approximately 3 microseconds it began again and ended with the burning of the spark (a_2). However, "attempts" to break off the discharge were observed many more times, which can be seen by the sharp breaks in the current. With an increase of voltage, the time of delay of 2 (Fig. I) accidentally turned out to be greater than 1. The temperature of the discharge channel was higher with an increase of current, and at the same time more charged particles were generated. This can be seen by the less deep breaks of current on Oscillograms III and IV (Fig. 115, I). Moreover, the breaks appear less frequently than during the recording of Oscillograms I and II.

The graduated-leader development of the breakdown was also recorded with a negative point (Oscillogram II,m). These oscillograms were also recorded with a gradual increase of voltage. A breakdown did not not follow during the recording of Oscillogram d, and only the current of conductivity was recorded.

After lengths of time of 148 and 155 microseconds there occurred almost complete breaks of the current $n_1$and n_2. But, after the laps of several microseconds, the gaps were breached again, and the discharges continued. These breaks were not registered in oscillograms of I because they appeared later. The same complete break of current even recorded with points (Oscillogram III, k). It is interesting to note that a break did not occur with the current $I_{maximum}$ equal to 0.57 amp. (Oscillogram II, n). The preparatory stage for the abrupt de-ionization was observed in place p (a smooth lowering of the current). The breaking of discharges is also apparently connected with the ejection of water from the inter-electrode gap as a result of increasing the pressure in the gas atmosphere of the discharge channel.

Oscillogram IV in Fig. 115 is presented in order to get some idea concerning the change of current during the burning of the spark in the silicon-organic liquid. The limiting resistance was equal to $r_0 = 5 \times 10^6$ ohms, but an additional non-inductive resistance $r = 5 \times 10^5$ ohms was switched on from the ground in order to record the current. For this reason, the abrupt surge of the current I_3' from the discharge of the capacitance of the electrode at the beginning of the process could not be recorded (see Fig. 111). As to the rest, the abrupt falls and rises of current corresponded to similar changes of voltage. Here there is graphically confirmed the hypothesis expressed above that there still remain many charged particles in the discharge channel after the abrupt de-ionization, and that for this reason the subsequent breakdowns form at comparatively low voltages. A complete breaking off of current did not occur in the whole period of discharge.

It is evident from the oscillograms of Fig. 114 that the characteristic physical-chemical properties of the liquids are reflected not so much in the sizes of the breakdown voltages as in the dynamics of their discharge after completion of the breakdown. In this period, with the appropriate limitations of the discharged current, there appears, as it were, the fine structure of the liquids, which is caused by the aggregate of the physical-chemical processes during the burning of the spark.

Inasmuch as part of the thermal energy which is released during the breakdown is usually expended on heating the electrodes, the temperature of the spark, the appearance of peaks, the time of cessation of the discharges, and several parameters must depend on the geometry of these electrodes, as well as on the length of the spark gap. In the case when the space charges have a noticeable influence on the dynamics of the discharge, the latter to some extent must also be determined by the degree of irregularity of the electrical field.

7-3. The Temperature of the Spark Channel in Liquids

Earlier, mention was repeatedly made of the temperature of the discharge channel in connection with action of thermal and photo ionizations, as well as pressure increase. It is known from the literature that the spark temperature can attain tens of thousands of degrees and more, for example, during breakdowns of gas gaps (L.265 - 268). With an electric arc, a considerable lower temperature usually develops in the air (L.269).

The temperature of the spark in air has been computed on the bases of calculation data, according to the Saha formula, concerning the concentration of ions of various degrees of ionization and the intensity of the lines of excitation of nitrogen in a time of 5×10^{-7} seconds (L.267). It proved to be equal to 4×10^{4} degrees K for a circuit with a capacitance of 0.25 microfarad and an inductance of 10 microhenry.

As of yet there are no data concerning the direct determination of the temperature of the spark in liquids. But there are some calculation material and experimental data concerming the individual parameters which determine the temperature. Its value computed according to these data also turned to be equal to several tens of thousands of degrees for transformer oil. (L.270).

The system of electrodes of the gap in question together with the supply mains, as was already noted, always forms a certain capacitance c. When the voltage on this capacitance increases from 0 to U_{br} there is accumulated the energy

$$Q_1 = \frac{0.24CU^2{}_{br}}{2} \text{ [cal]}, \qquad (51)$$

which is converted into thermal energy during discharge, and is also expended on radiation, ionization, and so forth.

At the moment of discharge the current $I = f(\tau)$, passes across the spark gap at a voltage U. Outside of depending on the principle of voltage lowering during the formation of breakdown, U_{br} can in practice be considered equal to 0 by the end of the process. And the current of normal conductivity I_0 increases from almost 0 up to $I_{maximum}$. In insulating liquids this current I_0 usually is many orders lower than $I_{maximum}$. For the sake of simplification it may be assumed that U and I change linearly during the time of formation and completion of the breakdown τ_1. Such an assumption will not lead to significant error because the voltage lowering during breakdowns of insulating liquids, as can be seen from Fig. 108, basically takes time τ_1, which is equal to the parts of the microsecond. Cases of the breakdown of long gaps without limitation of the discharge current are not examined here.

During the linear change of U and r

$$U = \frac{U_{br}(\tau_1 - \tau)}{\tau_1} \quad \text{and} \quad I = \frac{I_{max}\tau}{\tau_1}. \qquad (52)$$

In the discharge channel there is then released the thermal energy

$$Q_2 = \frac{0.24U_{br}I_{max}}{\tau_1^2}\int_0^{\tau_1}(\tau_1 - \tau_2)\tau d\tau = \frac{0.24U_{br/max}\tau_1}{6} \text{ (cal)} \qquad (53)$$

In so short a period of time τ_1 the electrons of the avalanches, in colliding with the molecules of the liquid, will ionize and excite them. For this reason, a considerable portion of the energies Q_1 and Q_2, during the process of formation of breakdown, will be accumulated at first in the narrow discharge channel of radius R as potential energy of the molecules (L.271). A state of equilibrium will be established only after the lapse of several tenths of a microsecond after the completion of this process.

It is known from experiments on the breakdown of air gaps that the gas is completely ionized in the spark channel (L.267 and 272). The same thing should also take place during the breakdowns of liquid dielectrics, inasmuch as the mechanisms of discharges are in many respects similar, especially in the limitation of the discharge currents (L.101 and 103). The complex molecules of liquid hydrocarbons, for example, transfomer oil, when heated to 600°C, already begin to decompose into more simple, gaseous ones (L.273), and at a temperature of 5000°C there occurs an almost complete dissociation of the molecules of H_2 and C_2 into atoms (L.274). But a very high pressure is formed at high temperatues in a closed spark channel. According to rough calculation, it can attain several hundreds of thousanas of atmospheres. This pressure will apparently stimulate the reunion of atoms and prevent the dissociation of gaseous molecules.

During the complete ionization of atoms or molecules, a plasma forms in the channel by the moment τ_2. It is known that Ohm's law is always satisfied for such a condition (L.275). Calculation for

$$\tau_2 = 10^6 \text{sec.}$$

The current of the discharge I_x after completion of the breakdown and the resistance of the spark channel r_x will change with the passage of time, but, for such a short time as $\tau_2 = 10^{-6}$ sec. they may be assumed to be constant. In the spark channel, then, there is released the additional amount of thermal energy

$$Q_3 = 0.24\int_{\tau_1}^{\tau_2} I_x^2 r_x d\tau \,(\text{cal}). \qquad (54)$$

The current I_x for the time $\tau_2 - \tau_1$ can be assumed to be equal to

$$I_x = N_0 ebE, \qquad (55)$$

where

N_0 - is the number of once-ionized particles in the space of the discharge channel;

e - is the elementary charge;

$b = b_+ + b_-$ - is the mobility of the current carriers;

E - is the field intensity after completion of the breakdown. This amount is usually small, but it can be determined according to the oscillograms with the help of an optical micrometer.

For the above-mentioned moment of time, it is possible, in the first approximation only the electron component of the current with a mobility $b = b_-$.

During the decomposition of complex molecules to simpler ones or into atoms, the number of charged particles in one cc will be equal to:

$$N_0 = \frac{N\gamma\Psi}{M}, \qquad (56)$$

where

N - is the Avagadro number;

M - is the weight of a single gram molecule of the liquid;

Ψ - is the number of new ionized particles into which the basic molecule decomposes;

γ - is the specific weight of the liquid.

And in the space of a discharge channel of cylindrical form with a radius of the base R and a length l, the number of such particles will be:

$$N_0' = \frac{\pi R^2 l N \gamma \Psi}{M} . \tag{57}$$

By substituting the value of N_0' from (55) into (57) the radius of the spark channel can be expressed as:

$$R^2 = \frac{M I_x}{\pi l \gamma N e b \Psi E} . \tag{58}$$

Inasmuch as a gas atmosphere is formed in the discharge channel, the Langevin formula (L.276), which has also been derived for gases, may be used for the mobility of the electrons:

$$b_- = \frac{e\lambda}{2m^* \overline{W}} , \tag{59}$$

where

e - is the elementary charge;

λ - is the length of the free path of the electron;

M^* - is its effective mass;

$\overline{W}$ - is the average speed of the thermal movement of the particles of the surrounding medium.

Substituting $\overline{W} = \sqrt{\frac{3kT}{m_0}}$ into (59), where m_0 is the mass of the particles of this medium, we will obtain:

$$b_- = \frac{e\lambda\sqrt{m_0}}{m^*\sqrt{3kT}} . \tag{60}$$

From (58) and (60) it follows that:

$$\frac{R^2}{\sqrt{T}} = \frac{M I_x m^* \sqrt{3k}}{\pi l \gamma N \lambda e^2 \sqrt{m_0}\ \Psi E} = B. \tag{61}$$

With the thermal capacity of the liquid c′ it is possible to write:

$$Q = Q_1 + Q_2 + Q_3 = \pi l \gamma c' R^2 (T - T_0). \qquad (62)$$

Disregarding the losses of energy and $T_0 \approx 200°K$ in comparison with T, from (61) and (62) the expression for the spark temperature can be reduced to the form:

(63)

The losses on radiant energy can be taken into account from

$$W_1 = 5.77 \cdot 10^{-5} T^4 (erg/cm^2 \cdot sec). \qquad (64)$$

Considering the spark to be a radiating black body, and disregarding the radiation from the side services of the channel, for $\tau_1 + \tau_2 = 1.1 \cdot 10^{-6}$ sec.:

$$W_1' = 5.77 \cdot 10^{-5} \cdot 2\pi R l (\tau_1 + \tau_2) T^4 \approx 4 \cdot 10^{-11} \sqrt{BT^{4.25}} \qquad (65)$$

The expenditure of energy on the dissociation of molecules and the ionization of the products of decomposition will be equal to:

$$W_4 = \left(\frac{W_2}{N} + W_3 \Psi\right) \frac{\pi l N \gamma R^2}{M} = DR^2, \qquad (66)$$

where

W_2 - is the energy of dissociation for 1 mole;
W_3 - is the energy of ionization for one molecule (atom);

The losses for the heating of the electrodes can be accounted for according to the number of collisions they have with particles. In comparison with the heat effect their acceleration in the electric field can be disregarded.

According to the Maxwellian law of distribution, part of the molecules with velocities in the ranges of v and v + dv can be determined, as is known, for a given direction according to the formula

$$\frac{e^{-\frac{mv^2}{2kT}}dv}{\int_{-\infty}^{+\infty} e^{-\frac{mv^2}{2kT}}dv} = \sqrt{\frac{m}{2\pi kT}}\,e^{-\frac{mv^2}{2kT}}dv. \tag{67}$$

The number of molecules or atoms q with mass m that strike a unit of the surface of the electrodes in a unit of time can be computed in the following way:

$$q = N_0\sqrt{\frac{m}{2\pi kT}}\int_0^{\infty} ve^{-\frac{mv^2}{2kT}}dv = \frac{N\gamma\psi}{M}\sqrt{\frac{kT}{2\pi m}}. \tag{68}$$

Inasmuch as the average kinetic energy of the particles moving perpendicular to the surface is equal to dT, then, in collisions with the electrodes, the particles will transmit to them an energy of $qk(T - T_1)$.

It is possible to consider that T_1 = const (290°C) for the time τ_2 when the mass of the electrodes is considerable. There area, where the collisions must take place, is equal to πR^2, and the energy transmitted to them is

$$W_5 \approx qk(T - T_1)\tau_2\pi R^2. \tag{69}$$

After the substitution of R^2 from (61) the expression of (69) will take the following form:

$$W_5 = \frac{2\pi k(T - T_1)\tau_2 N\gamma\psi B}{M}\sqrt{\frac{k}{2\pi m}}\,T = \Phi B(T - T_1)T, \tag{70}$$

where $\Phi \approx 1.76 \cdot 10^4$. Moreover, some energy will be expended on the formation of the shock wave, as even happens during the breakdowns of gas gaps (L.277 and 278), as well as on the heating of molecules located near the channel. These losses are not considered in further calculations.

Subtracting the losses of (65), (66), and (70) from (62), we obtain

$$Q - 4\cdot 10^{-11}\sqrt{B}\,T^{4.25} - \Phi B(T - T_1)T - DB\sqrt{T} = \pi l\gamma c' BT^{1.5}. \tag{71}$$

From this equation the temperature of the spark can be determined graphically.

The values of $I_{maximum}$, I_x, r_x, E and U_{br} in (71) are determined from the already known parameters of the plan of Fig. 111, as well as from the oscillograms of the breakdown and the post-breakdown discharge. The length of the free path of the electrons without corrections for the temperature and travelling speed can be determined from the known formula

$$\lambda \approx \frac{1}{\pi r^2 N_0},$$

where r is the radius of the molecules or atoms.

It can also be roughly assumed that the diameter of the discharge channel and the number of molecules in one cc (N_0) will remain unchanged for a time close to one microsecond. Under this condition

$$\lambda \approx \frac{M}{\pi r^2 N \gamma \Psi}. \qquad (72)$$

According to roughly approximately calculations and experimental data, the spark temperature in transformer oil which has been cleaned by 30% fuming sulfuric acid proved to be equal to approximately 4.2 times 10^4 °K, while the radius of the dischage channel was $R = \sqrt{B\sqrt{T}} \approx 1.1 \cdot 10^{-4}$ cm (L.270).

The calculation was carried out on the assumption that the complex molecules of the transformer oil only decomposed into CH_4.

If the molecules of the transformer oil decompose into atoms at a temperature greater than 5000°C, even with extermely high pressures in the discharge channel, then the temperature conditions of the spark will change. Such decomposition is usually accomplished during large expenditures of energy ($W_{\pi} = 1.03 \cdot 10^5$ and $W_c = 8.3 \cdot 10^1$ cal/mole). For this reason, the spark temperature during decomposition should drop noticeably. And it is apparently highest, as during the breakdown of gas gaps, in the initial stage of discharge (L.277). But, at a certain critical value of it, when the process of reunion of atoms into molecules begins, this temperature can again noticeably increase from the release of energy.

The pressure in the discharge channel will also lower with its reduction. If before this the plastic properties of the liquid have not had time to appear, and only the elastic contraction of the molecules like a spring has occurred, the sign of the pressure can change to the opposite one; the ejection of the liquid will not occur. But in this case, if the plastic properties of the liquid have had time to appear, and expansion of the gas in the space in the channel has occurred, a vacuum can form there when the temperature is lowered. Non-ionized molecules then penetrate into the area of the channel under the influence of the outside pressure, and the discharge may break off temporarily or finally.

7-4. The Pressure in the Discharge Channel

It has already been mentioned above that the pressure of the gaseous medium in the discharge channel rises sharply at high temperatures. Ejections of liquids occur for the above mentioned reason, and in some cases there arise crushing forces which are transmitted to the walls of the measuring vessels. In this case the spark acts as an explosive.

In this work (L.279) an attempt has been made to determine the efficiency during a similar conversion of electrical energy into mechanical. A capacitor with a capacitance of from 0.012 to

0.07 microfarad charged to a voltage of from 12 to 18 kv was discharged across a spark of a sliding discharge along a Pertinax plane which had been placed in water. In this case the mechanical forces were transmitted to a bob by a weight of from 2 to 20 grams which had been separated from the water by a thin sheet of mica. The height of the bouncing of the bob was equal to from 50 to 250 cm. The efficiency which was determined from comparing the work of this bob and the accumulated energy in the capacitor proved to be equal to around 1%.

The transmission of mechanical forces by the real compressible liquids occurs through the shock wave. The liquid compresses in the places of pressure application. Its density increases, and the compressed condition shifts from the place of origin of the pressure to the periphery. This compressed section is called the front of the shock wave. It can move with supersonic speed. At large distances the shock wave degenerates into a sonic one.

It has been established in studies of gas discharges that there is a sharp drop of density in the casing of the discharge channel. The density of the gas is low in the disturbed region from the center of the channel almost up to the front of the shock wave, but is sharply increases at the front. Further on, it drops abruptly (L.280).

The speed of the shock wave in water and the density of the substance at the front were determined in (L.281). The water was poured into a cylindrical vessel ($h = 5$ cm) which was made of cellophane. Lead plates were set at intervals of 1 cm along all the height of the cylinder. An explosive was detonated below through a percussion cap, and a pressure equal to approximately 2.5 times 10^5 atmospheres was created. The water was compressed, and this compressed condition (the shock wave) shifted upward. An X-ray tube was turned on simultaneously with the explosion, and the rays penetrated the cylinder with water. The greater was the density of the liquid, the greater was the number of rays absorbed, and they were absorbed almost completely by the lead plates. These rays then fell on film, and it was even possible to determine the speed of the shock wave according to those lead plates around which the most dense sections were found. It turned out that the density of the water was equal to 1.75 at its front. The initial speed of the wave did not exceed 6600 m/sec. At a distance of approximately 40 mm from the place of the explosion its speed decreased to approximately 1500 m/sec. The pressure also decreased sharply.

In this work (L.282), the question of getting cumulative currents of a liquid in a converging flow of sufficient density is examined. It has been observed that such a current can be obtained not only by explosives, but also be the ejection of a liquid at the moment of discharge across the spark of a capacitor with a capacitance of 1000 ohms at a difference of potentials of several tens of kilovolts.

Besides ejections of liquids, the existence of a strong spark brisance has been discovered by the author of large gaps of distilled water and transformer oil without limitation of the discharge current. After several breakdowns the heavy porcelain vessels with a wall thickness greater than 20 mm broke (L.242). The same thing was also observed in discharges of a battery of capacitors $C = 9.8$ microfarad onto a thin copper wire $d = 0.1$ mm and $l = 55$ cm which had been placed in glass pipes with water and transformer oil. The capacitors discharged up to from 70 to 80 kv. In this case the pipes were crushed to small pieces (L.283).

It is well known that the destruction of material occurs considerably more easily with the quick application of forces. This particularly concerns the perforating effect. A successful attempt was made to apply those forces which arise during discharges in water to make holes in very solid substances (L.284). There is a report about the transmission of signals in water from the place of discharge in (L.285). The gap between electrodes of l = 5 cm was breached. At a distance of around 100 cm from the spark, acoustic impulses were recorded by piezoreceivers made of ceramic barium titanate. It has been established that in this case the conversion of electrical energy into acoustic energy occurs with an efficiency up to 30%. In the case of a constant l the effectiveness of energy conversion decreases if the store of electrical energy is raised by an increase of the capacitance of the discharging capacitor with the voltage unchanged.

Studies have been devoted to determining the amounts of the pressures in the discharge channel during the breakdown of water (L.286 and 287). Gaps of l equal to from 1.2 to 1.5 cm between points were breached. There was discharged across the breached gap a battery of high-voltage capacitors with a capacitance of from 2.7 to 240 microfarads which had been charged with a voltage of from 12 to 40 kv. In this case currents of from 12 to 750 ka passed across the spark channel, and the speed of their increment changed from 3.6 times 10^9 up to 1.75 times 10^{11}amp/sec. During the experiments the currents were measured by a Rogowski loop, and the discharges were recorded by a cathode oscillograph and photographed by equipment with revolving mirrors. The speed of turning was equal to 60,000 rpm.

It has been shown that, if the glowing bridge between electrodes is considered to be the channel, then the density of the current in the channel is equal to 1.2 times 10^6 amp/cm^2. But the authors consider this number to be deliberately underestimated, since their exists a transitional layer of excited gas between the strongly heated channel and the cold liquid, where an insignificant portion of the current flows.

At a speed of current increase of 3.6 times 10^9 amp/sec, the speed of motion of the front of the shock wave P was found to be equal to 1600 mm/sec, and the speed of spread of the channel was $V_k \approx 200$ m/sec. After from 0.5 to 1.5 microseconds the front of the shock wave breaks away from the channel and moves on with a constant speed. The even expansion of the discharge channel also takes place at this time.

For the case of cylindrical symmetry, calculation of some parameters during discharges was carried out on the assumption that the water between the front of the wave and the channel can be considered incompressible and to have the same density ρ as is at the front ($\rho = \rho_\Phi$). Certain other simplifying assumptions have also been made.

From the continuity equation for the speed of the water v at a distance r we may write:

$$v = \frac{v_\Phi r_\Phi}{r}, \tag{73}$$

where

v_Φ - is the speed of the water behind the wave front;
r_Φ - is the radius of this front.

The relation between r_Φ and the radius of the discharge channel r_k was obtained from the condition of the preservation of the mass of the water disturbed by the shock wave:

$$\pi r_\Phi^2 = \pi a(r_\Phi^2 - r_k^2), \tag{74}$$

where $a = \frac{\rho_\Phi}{\rho}$ is the compression of the water by the shock wave;

ρ_0 - is the initial density of this water.

From (74) the relationship of the radii will be equal to:

$$\frac{r_k}{r_\Phi} = \sqrt{\frac{a-1}{a}}.$$

The speed of expansion of the channel V_k can be determined from the correlation

$$V_k = \sqrt{\frac{a-1}{a}}\,D = \sqrt{\frac{a}{a-1}}\,V_\Phi. \tag{75}$$

The authors determined the relationship between the pressure of the water P at a distance r and the pressure at the front P_Φ from the Eulerian equation for an ideal liquid (L.288):

$$\frac{\partial v}{\partial t} + (v\nabla)v = -\frac{1}{\rho}\,\mathrm{grad}\,P.$$

After substituting (73) into thie equation and integrating for P, an expression of the following form was obtained:

$$\frac{P}{\rho_\Phi} = \frac{P_\Phi}{\rho_\Phi} + V_\Phi D \ln\frac{r_\Phi}{r} + \frac{1}{2}V_\Phi^2\left[1-\left(\frac{r_\Phi}{r}\right)^2\right]. \tag{76}$$

From the already known correlation for the shock wave

$$V_\Phi^2 = D^2\left(\frac{a-1}{a}\right)^2 = \frac{P_\Phi}{\rho}\left(\frac{a-1}{a}\right)$$

and from (74) the pressure at the boundary of the spark channel is determined:

$$P_k = \frac{P_\Phi}{2}\left(1 + a\ln\frac{a}{a-1}\right). \tag{77}$$

The interdependence between P_Φ and a is determined from the equation of the adiabatic curve of the shock for $P_\Phi < 8\cdot10^4$ atm.:

$$P_\Psi = 3050(a^{7.15}-1).$$

The speed of the shock wave and the speed of epansion of the discharge channel as computed according to the derived formulae turned out to be in satisfactory agreement with the experimental data.

With a certain simplification with regard to the form of the energy pulse, it is suggested that the pressure at the front of the shock wave in (L.289) be computed according to the formula

$$P_{\Phi} = \frac{\beta}{T} (\rho W)^{1/2} B, \tag{78}$$

where

ρ - is the density of the liquid;

W - is the complete pulse energy per unit of length of the channel;

T - is the length of the energy pulse;

- is the function of the relationship of the thermal capacities.

If the length of the front is symbolized by Θ, then for a time $\tau \leqslant \Theta$ the amount of $B = \left(\frac{\Theta}{T}\right)^{-1/2}$.

From an analysis of this formula it is concluded by the author (L.289) that the pressure P_{Φ} grows with an increase of the density of the liquid and the total energy of the pulse, as well as during a decrease of the overall length of its front. Calculations of P_{Φ} according to (78) provides values that are more overstated (by 4 to 5 times) than according to (77)(L.287).

But gas laws can be used for a rough determination of the pressure in a closed discharge channel with a gas atmosphere. Let us examine the behavior of a gas in a closed cubic vessel with a length of walls of Δl. An individual molecule flying with a speed v perpendicular to one of the walls collides with it and rebounds back. In this case the amount of motion of the molecule equal to the impulse of the force changes by an amount $2mv = \Delta F \delta\tau$ where $\delta\tau$ is the duration of the shock, and ΔF is the force.

According to Newton's third law, the wall should be acted upon by a force which can be represented as acting continuously for a time $\Delta\tau$ which is necessary for the molecule to fly to the opposite wall, rebound off it and return back. Its force $\Delta\bar{F}$ will be less than ΔF, but the impact should be the same:

$$\Delta F \Delta\tau = 2mv;$$

however

$$\Delta\tau = \frac{2\,\Delta\,l}{v}$$

and

$$\Delta\bar{F} = \frac{mv^2}{\Delta l} .$$

The other molecules of n will move with different speeds v_1, v_2 ... v_n, and the force of the impact will be determined by their sum;

$$\Delta F = \frac{1}{3} \cdot \frac{nm\overline{v^2}}{\Delta l} , \tag{79}$$

where $\overline{v^2}$ is the average value of the squares of these speeds.

The number of molecules moving between the front and back walls is assumed to be equal to 1/3 n. If both parts of (79) are divided by Δl^2 (the area of the wall), then $\frac{F}{\Delta l^2}$ will be equal to the pressure upon this wall, and $\frac{n}{\Delta l^2}$ will be equal to the number of molecules in a unit of volume N_0. For this reason

$$P = \frac{1}{3} N_0 m v^2,$$

but

$$\frac{mv^2}{2} = \frac{3}{2} kT \text{ и } P = N_0 kT. \tag{80}$$

When replacing N_0 from (56) for the pressure in the discharge channel we get:

$$P_k = \frac{N\gamma kT}{M}. \tag{81}$$

By substituting into (81) the values of T for transformer oil from the preceeding section, we get P_k $1.3 \cdot 10^5$ atm. This amount is close to the pressure which was computed according to the formula (78). There is no doubt that at such large pressures expansion of the channel will at first occur due to compression of the liquid. In this case the pressure will lower. In very small segments of time, as has been noted, a state of liquid viscosity may not yet form, and the energy of compression will be in the form of potential energy of molecules.

It should be noted that such compressions can be considerable, even in as poor a compressible as water. An idea of this can be obtained from Table 49 (L.290).

Table 49

Volumetric decrease of water for various pressures and
and temperatures -- 0.50 and 95°C

pressure kg/cm²	0° C	50° C	95° C
0	1,0000	1,0119	1,0395
1 000	0,9567	0,9741	0,9984
5 000	0,8626	0,8824	0,9009
10 000	—	0,8192	0,8352

It is known that tangential elasticity cannot be observed in the case of slow deformations, because the viscosity is great. But with the rapid action of an outside force the viscosity is almost unnoticeable at the first instant, whereas the elasticity appears to its full extent (L.291). As far back as Maxwell it has been assumed that the speed of resorption, or the relaxation of tangential forces arising in liquids during the action of this force, is proportional to its size (L.292). From the solution of the differential equation during harmonic conditions of deformation it is proven that a liquid can behave as a solid body when there is a very quick application of force. In this work (L.293) it is shown that even a brittle shattering is observed in liquids under these circumstances.

The high pressure within the discharge channel evidently arises within a period of several tenths of a microsecond. After this, at some definite moment, the liquid will behave like a solid body, and, in spite of the high pressures, its ejection will occur only after the lapse of some time, as was observed. Apparently, this should be characteristic for each liquid taken separately.

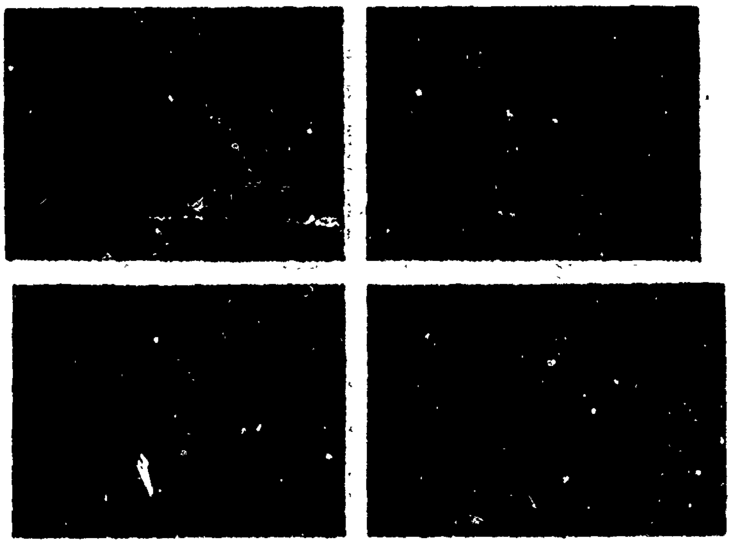


Fig. 116. Oscillograms of the breakdown of liquid dielectrics with a positive and plane.

Such discharges are usually extremely intense during the breakdown of transformer oil and xylene without great limitations of the discharge current. They break off the discharges at still comparatively large voltages. But in the case of breakdowns of liquids of great viscosity, such as a solution of ethyl celluse in toluene and pentadichloradiphenyl, ejections are not observed, and the discharge after the initial breakdown continues almost until the end of the action of the implied impulse. The corresponding oscillograms are presented in Fig. 116. They were recorded during breakdowns of a gap of [illegible] between a positive and a plane. The period of the sinusoidal oscillations on the axes of the abcissas is equal to 44 microseconds. The discharge current did not exceed 1.3 amp. Explanations of the oscillograms are given in Table 50.

Table 50. Explanation of oscillogram in Figure 116.

Oscillogram no.	Liquid	Initial breakdown voltage	Time of rapid deionization occurence µsec	Discharge attenuation time µsec
I	Transformer oil	12.0	370	>2000
II	Xylol	14.0	400	400
III	6% solution ethylcellulose in toluol	8.0	-	>1500
IV	Pentachlorodiphenyl	14.8	-	>1500

According to Oscillograms I and II, the time during which the plastic properties (viscosity) of the transformer oil and xylene could appear is approximately equal to 370 and 400 microseconds. At a distance between balls of 0.2 mm this time in xylene was equal to around 250 microseconds according to Oscillogram I of Fig. 110. The above-mentioned difference must apparently be attributed to the.difference must apparently be attributed to the different pressures in the discharge channel.

In Illustration I of Fig. 116 Oscillogram A was recorded without breakdown of the gap, while Oscillogram B was recorded with breakdown. After abrupt de-ionization of the channel and an increase of the voltage to 4.5 kv the transformer oil was breached again. Voltage peak V was formed, after which the discharge continued more than 2000 microseconds. But such repeated breakdowns do not always form. In approximately half the cases the discharge after abrupt de-ionization breaks off once and for all, as in the breakdowns of xylene (see D of Oscillogram II).

Apparently the forces of cohesion of the molecules in the solution of ethyl cellulose in toluene and the solution of pentachlorodiphenyl were great, and in the comparatively short time of the action by the high pressure the plastic properties did not have time to appear. It must, however, be noted, that the questions under consideration are almost completely unstudied.

CHAPTER EIGHT

THEORIES OF BREAKDOWN TAKING INTO ACCOUNT THE INFLUENCES OF TEMPERATURE, DISSOLVED GASSES AND MOISTURE

8-1. Some Notes on Breakdown Theories

The breakdown of liquid dielectrics as was shown above is characterized by extremely complex phenomena. Therefore the development of some general theory of breakdown, in which we would find the reflection of all the necessary irregularities can be considered an extremely complicated matter. Authors of the existing theories generally have not attained to such a goal, either. As a rule it has become a more restricted problem - to explain only a few regularities or only one of them. Many theories, moreover, give only the qualitative character of one regularity or another. It is well known that in the past several decades the theory and practice of gaseous discharge has mushroomed. In the development of the theoretical concept of the breakdown of liquid dielectrics much has been accomplished in bringing from that which was earlier was obtained just in an investigation of the electrical strength of gases. Such relations were extremely useful, for example, for understanding of the processes of impact ionization, field distortion by space charges, etc.

The structure of liquid dielectrics is still weakly studied and this is the basic lag for the extinction of a more general theory of electrical breakdown. As is known, the structure of solid crystal dielectrics is studied significantly better. This to a significant degree has also facilitated the development of breakdown theory, for example, of alkaline helogen crystals. The calculated and experimental values of their breakdown strength were closely coincident (L.294-296). This success exerted a certain influence also upon the development of the theory of electrical breakdown of liquids. It was shown for example that the breakdown strength of carbon tetrachloride can be determined by formulas derived for aklaline helogen crystals. The experimental and calculated value of E_{br} in this case also offered a satisfactory correspondant.

8-2. The Gas and Gas-thermal Theory of Breakdown of Liquid Dielectrics

Attention has been paid for a long time to the circumstance wherein in a liquid after undergoing stress in the determined condition, gas bubbles are formed. It was noted that their appearance affects the development of the breakdown (L.297 and 298). These experimental facts served as starting points for Gemant's construction of a theory of breakdown of isolated liquids (L.299 and 300).

According to this theory the breakdown is formed not in the liquid but in the bubbles which are formed from the accluded electrodes and the fluidity of the gas. Gas bubbles at the electrodes are charged with the same sign as the electrode. The electrical field distends them and changes the energy. By such extension the force of the surface tension is impaired.

For simplifying the problem only two conditions are examined:

1) when the volume of the bubbles remains unchanged in their extension, i.e., the height of the bubble is increased and the area of the base diminishes;
2) when the area of the base remains unchanged but in elongation the volume is increased. This increase, according to Gemant's assumption can take place on account of supplementary portions of gas drawn into bubbles from the electrode. It is further postulated until deformation has the form of a hemi-

sphere of radius r and after extension the form of a semi-ellipsoid with the major axis a'.

The energy of deformation of the bubble W can be set equal to:

$$W = \alpha W_1 + \beta W_2, \tag{82}$$

where α and β - are coefficients characterizing the change in volume;

W_1 - is the energy of deformation of the bubble in a constant volume;

W_2 - is the same, but with a constant base.

In the case where in the distortion of the bubble its energy is increased and

$$\lim_{\mu \to 1} \frac{\partial W}{\partial \mu} > 0,$$

then the deformation does not occur at all. And if

$$\lim_{\mu \to 1} \frac{\partial W}{\partial \mu} < 0,$$

then the equilibrium will be destroyed and the deformation follows. In the expressions just derived $\mu = \frac{a'}{r}$ denotes the degree of deformation. The change in sign of the derivative will be determined by the quantity of applied voltage E_1. This change is taken for criterion of the beginning of the test. Consequently E_1 may be considered to be the breakdown voltage.

The energy of the bubble deformation W (82) depends upon the electrical energy W_1', the surface energy W_1'', and also the work against the forces of W_1'''. For the electrical energy when the deformation of the bubble takes place with a constant volume, one can write:

$$W_1' \approx - \frac{r^3 E^2}{6 \frac{1-e^2}{e^3} \left(\frac{1}{2e} \ln \frac{1+e}{1-e} - 1 \right)}, \tag{83}$$

where $e = \sqrt{1 - \frac{1}{\mu^3}}$ is the eccentricity of the ellipsoid.

The energy with a constant base

$$W_2' \approx \frac{\mu V E^2}{6\frac{1-e_1^2}{e_1^2}\left(\frac{1}{2e_1}\ln\frac{1+e_1}{1-e_1}-1\right)}; \tag{84}$$

here

$$e_1 = \sqrt{1 - \frac{1}{\mu_2}} \ :$$

The surface for the first case is equal to :

$$W_1'' = \gamma\left[S + \pi r^2\left(1-\frac{1}{\mu}\right)\right], \tag{85}$$

and for the second:

$$W_2'' = \pi\gamma r^2\left(1+\frac{\mu}{e_1}\arcsin e_1\right); \tag{86}$$

In these formulas γ is the coefficient of surface tension and S is the surface of the semi-ellipsoid.

The work against the pressure forces for the first case can be expressed thusly:

$$W_1''' = 0.$$

and for the second:

$$W_2''' = \frac{2\pi}{3} r^3 \mu P; \tag{87}$$

here P is the pressure in the bubble.

The breakdown voltage is found from the expression of the maximum total deformation energy W with $\mu = 1$:

where $\frac{\beta}{\alpha} = n$, we obtain: $\lim\limits_{\mu \to 1}\frac{\partial W_1}{\partial \mu} + n\lim\limits_{\mu \to 1}\frac{\partial W_2}{\partial \mu} = 0.$

(88)

The coefficient n depends upon the viscosity μ of the substance studied. With an increase in μ the probability of deformation with a constant should also increase.

Inserting in (88) the vaules of W_1 and W_2 from the foregoing equations (83), (84), (85), (86), and (87) for the breakdown voltage with $n = \frac{k}{\eta} < 0.1$ we obtain an expression (in absolute value):

$$E_{br} = \sqrt{\frac{10\pi}{3}\left(\frac{\gamma}{r} + \frac{2}{3} + \frac{k}{\eta}P\right)} \quad , \qquad (89)$$

where k is a constant independent of η.

The breakdown voltage calculated from formula (89) in some coincides with experimental values. Its formula relates E_{br} to the viscosity of the liquid, its gas content, and also with the gas content of the electrodes and the pressure in the bubble. The details of the breakdown mechanism remain unknown. Apparently it can be considered that the expression (89) will be more satisfactory for small distances between electrodes when one bubble in distortion may overlap the entire interelectron interval.

According to Edler's theory (L.301) an electrode with occluded gas bubbles may be considered separate from a liquid of the thin gas layer. It is understood that the electro-conductivity and the heat conductivity of the layer is less than it is in the liquid. In such a layered dielectric the applied current is determined by the inverse of the conductivity. Edler showed that the greatest temperature in the equilibrium state will be on a boundary between the gas layer and the liquid layer. The voltage of the applied field is taken into account by the breakdown voltage in which the indicated temperature is raised to so much that the liquid begins to boil.

The amount of heat evolved per unit of time with flat electrodes, the current I and the voltage U, will be equal to

$$IU = f(U)U = I^2R; \qquad (90)$$

here $I = f(U)$ is the known dependence of current upon voltage;

R - is the sum of the distances of the liquid and the gas layer.

In specific resistances of the layer ρ_1 and of the liquid dielectric ρ_2 the overall resistance in (90) may be presented thusly:

$$R = 2[\rho_1 a + \rho_2(h-a)] = A\rho_1,$$

where a - is the thickness of the gas layer;

2h - is the separation between electrodes.

The quantity of heat evolved in the gas layer will then be equal to:

$$I^2\rho_1 = \frac{1}{A} Uf(U). \qquad (91)$$

If this heat is equal to the outgoing heat, then

$$I^2\rho_1 = \text{div } q,$$

where q is the amount of heat transmitted per unit to a unit of surface.

In the layer the temperature T and the coefficient of heat conductivity of the gas layer k_1

$$q = k_1 \text{grad } T;$$

$$I^3\rho_1 = -k_1 \text{div} \cdot \text{grad } T. \qquad (92)$$

For the one-dimensional case with a sufficiently large area of the electrodes, it follows from (93) that:

$$I^2\rho_1 = -k_1 \frac{d^2T}{dx^2}.$$

The solution of this equation relative to the gas layer yields:

$$T = -\frac{1}{2} I^2 \frac{\rho_1 x^2}{k_1} + C_1 x + C_2. \qquad (93)$$

The constants C_1 and C_2 may be determined from the boundary condition.

With a continuous process and x = a or X § 2h -a

$$k_1 \left(\frac{dT}{dx}\right)_{x=2h-a-0} = k_2 \left(\frac{dT}{dx}\right)_{x=2h-a+0},$$

where k_2 is the heat conductivity of the liquid.

If we set x = 0 or x = 2h and designate the temperature of the electrode as T_0, the following equality is obtained:

$$T = T_0.$$

If the heat evolved in the dielectric is negligeable compared to the heat in the gas layer around the electrode and with $k_2 >> k_1$, and also $\rho_2 << \rho_1$, according to Edler we can take divq = 0. With these assumptions the values of C_1 and C_2 are determined from

$$C_1 = \frac{Ba\rho_1 I^2}{k_1} \quad \text{и} \quad C_2 = T_0;$$

$$B = \frac{1 - \frac{k_2 a}{2k_1(2h - a)}}{1 - \frac{k_2 a}{k_1(2h - a)}} \approx 1,$$

and the equality (93) may also be written in the following form:

$$T - T_0 \approx \frac{I^2\rho_1}{k_1}\left(ax - \frac{1}{2}x^2\right).$$

On the boundary of the liquid and the gas with $x \approx aT = T_{max}$. For this case

$$I^2\rho_1 = \frac{2k_1}{a^2}(T_{\text{макс}} - T_0) = U_{\text{пр}} f(U_{\text{пр}}). \tag{94}$$

As was already noted, for the breakdown criteria of Edler the condition was taken in which T_{max} is equal to the boiling temperature: $T_{max} = T_{knp} = f(P)$ where P is the pressure. The experimental curves of the function $U_{br} = f(T_{knp}, P)$ agreed with the theoretical curves.

The spacing between the electrodes enters into a and $f(U)$. According to Edler, $\frac{\rho_2}{\rho_1} = 10^{-7}$. The value of $\rho_2(h-a)$ in comparison to $a\rho_1$ and the dependence between U_{br} and h is simplified.

The time τ from the beginning of the voltage untill the breakdown may be determined from the expression for the quantity of heat Q which must be expended to bring the liquid to a boil:

$$Q = (T_{knp} - T_0)c_0 d, \tag{95}$$

where c_0 is the heat capacity; d is the specific weight.

On the other hand, $Q = I^2 \rho_1 \tau$; therefore

$$\tau = \frac{(T_{knp} - T_0)c_0 d}{I^2 \rho_1}. \tag{96}$$

Thus, from Edler's formula one can determine U_{br} as a function of the separation between the electrodes and the time of exposure or the length of time the voltage is applied.

As a basis of both theories highly simplified and not entirely concepts on the physics of the breakdown phenomemon are set down. It was already noted above that in Gemant's theory impact ionization is not taken into account. Edler's theory is based primarily on the examination of thermal processes. Basically neither one reflects modern views on the breakdown mechanism. However, the concept of the important role of gas bubbles in the formation of the breakdown of liquid dielectrics even now has not lost its meaning.

8-3. The Heat Theory of Breakdown

As is known, a liquid heats up when a current passes through it. Its volumetric specific resistance is reduced, and the current increases. If the heat outflow form the interelectrode gap is sufficient, then the temperature of the liquid will be progressively increased until breakdown.

It is known from experiments that increasing the temperature until the liquid boils, its breakdown is strongly reduced (See Fig. 20), The field strength, in which the boiling begins, is taken for the breakdown voltage in a theory of Semenov and Val'ter (L.302). The parameters determining the process of breakdown formation of liquids in this theory have the following designation:

Q - is the amount of heat evolved in the liquid during 1 second in a field intensity E;
Q_2 - is the amount of heat going out during the same period by the mechanisms of heat conductivity and convection;
T - is the temperature in a more heated local section between the electrodes;
T_0 - is the temperature of the medium surrounding this portion.

According to the assumptions of the authors indicated:

$$Q_1 = aE^n \tag{97}$$

and

$$Q_2 = b(T-T_0); \tag{98}$$

In these equations a and b are proportionality constants. Here it is also assumed that when the liquid is boiling, a gas bridge is formed between the electrodes, in which the breakdown formation also begins. Of course, the condition:

$$Q_1 > Q_2 \qquad (99)$$

$$Q_1 = Q_2 + \theta$$

should without fail be satisfied. Here θ is a positive quantity.

From (97), (98), and (99), it follows that:

$$aE_{br}^n = b(T_{knp} - T_0) + \theta$$

and

$$E_{br} = \sqrt[n]{A(T_{knp} - T_0) + B}. \qquad (100)$$

From equation (100) one can establish a qualitative dependence of E_{br} upon the temperature. During an increase of T_0 the value of E_{br} should increase. Inasmuch as the boiling temperature T_{knp} is generally determined by the pressure P, the dependence $E_{br} = f(P)$ can also be established. Cooling the liquid or the heat going out in the electrodes may decrease with an increase in the inter-electrode distance. Consequently formula (100) includes also the dependence $E_{br} = f(l)$; carrying away the heat in the electrodes already suggests the dependence E_{br} upon the material of the electrodes, because the heat conductivity of the metals is generally not the same.

Formula (100) evidently cannot be extended to a short applied voltage duration. It is possible, of course, to confirm that for a quick increase in Q_1 it is necessary to increase E, but the mechanism of breakdown formation may change in this.

The same formula for E_{br} as in (100), is introduced more than thirty years later by Sharbo and Divins (L.303). Their theory is based upon experiments a description of which is given in (L.221). The authors indicated consider that with $E = 1.6$ mv/cm, even in the case where short impulses are connected, the heat evolved is sufficient for local boiling of n-hexane and formation of gas bubbles.

Calculations showed that when applied to liquid hydrocarbon of the paraffin series the coincidence of data calculated from formulas (100) and experimental data of E_{br} is good when $n=3/2$.

A more valid approach to an explanation of the mechanism of the heat-up of liquid is made by Guenterschultz (L.304 and 305). Each dielectric, as is known, has a volumetric conductivity. When the voltage is switched on an ion moving between the electrodes in a viscous medium should experience a certain friction. The greater this friction, the greater the heating of the liquid will be. At a certain voltage E the liquid boils and behind the moving ion a submicroscopic gas path is created, in which a discharge may occur.

From experience it is known, that E_{br} is increased in increase of pressure upon the surface of the liquid. This circumstance is treated here as a change in the length of the free-moving electron in the gas canal and it is asserted that with a sufficiently low pressure and corresponding voltage ions in the gas canal may accumulate energy between two collisions sufficient for ionization. It may be noted that this assertion is the weakest point of the theory.

Let us assume that the pressure on the surface of the liquid is equal to zero ($P = 0$) and that the breakdown is formed as soon as the gas canal is formed. Now if this pressure is increased then the length of the free path will be decreased and for a breakdown, E must be increased:

$$E_{br} = E_{knp} + \Delta E$$

where $$\Delta E = f(P).$$

It is known that $\lambda = \frac{k}{P}$, therefore:

$$E = \frac{W}{\lambda e} = \frac{WP}{ek} = aP, \tag{101}$$

where k and a are coefficients; W is the kinetic energy of the ion to the end of one free path; E is the charge of the ion.

Therefore,

$$E_{br} = aP + E_{knp} = aP + b. \tag{102}$$

According to the data of Section 2-3, it follows that with pressures greater than atmospheric pressure E_{br} increases non-linearly and asymptotically approaches a certain limiting quantity E_{max} (see Fig. 21 and 22). The corresponding E_{max} pressure P_0 does not exceed several dozen atmospheres. In comparison with the inside pressure of the liquids (approx. 2000 atm), P_0 is insignificantly small and can hardly change the average length of the free path of the ion.

8-3. A Theory of Breakdown Taking Into Account the Influence of Moisture

In the account of experimental data of the influence of the addition of water upon U_{br}, it was shown that isolated liquids may contain water both in a dissolved molecular state in emulsions; the most dangerous of which concerning a reduction of U_{br} being the emulsified state.

For an explanation of the mechanism of reducing U_{br} in wetting liquid dielectrics, Gemant (L.75) suggested one more theory, according to which the breakdown is formed along a conducting bridge of suspended and polarized water canals. Thus, this theory may comprise also the emulsified state of water in liquids.

When a constant voltage is switched on, round water drops may also be deformed and assume an elliptical shape. In a corresponding field intensity which is assumed to be homogeneous they form a dense water canal with an increased conductivity. The extension of the drops is characterized by the levation of their initial radius in the absence of a field when they had a spherical shape to the major axis of an ellipsoid after their distinction by the field.

The overall energy of the polarized ellipsoid, as is known, is equal to $W = W_1 + W_2$ where W_1 is the energy of the surface tension of the ellipsoid of revolution, and W_2 is the polarization energy. The first component may be written in the following manner:

$$W_1 = 2\pi r^2\gamma\left(\sqrt{1-e^2} - \frac{\arc \sin e}{\sqrt{1-e^2}}\right) \qquad (103)$$

where γ - is the coefficient of surface tension on the boundary of the water and the liquid of the dielectric;

r - is the radius of the drop in spherical shape until deformation;

e - is the eccentricity.

The second component W_2 in a homogeneous field intensity E and electrical moment of the ellipsoid P_0 is equal to:

$$W_2 = -\frac{1}{2} P_0 E, \qquad (104)$$

and

$$P_0=\frac{4}{3}\pi r^3\frac{\frac{\varepsilon-1}{4\pi}E}{1+(\varepsilon-1)\frac{1-e^2}{e^2}\left(\frac{1}{2e}\ln\frac{1+e}{1-e}-1\right)}, \tag{105}$$

where ε is equal to the ration of the dielectric permeability of the gas in a spherical cavity ε′ and liquid ε′′.

Therefore, the total energy from (103), (104), and (105) can be presented in the following form:

$$W=2\pi r^2\gamma\left\{\left[\sqrt[3]{1-e^2}-\frac{\arcsin e}{e\sqrt[6]{1-e^2}}\right]-\frac{\frac{\varepsilon-1}{4\pi}\cdot\frac{r}{3\gamma}E}{1+(\varepsilon-1)\frac{1-e^2}{e^2}\left(\frac{1}{2e}\ln\frac{1+e}{1-e}-1\right)}\right\}. \tag{106}$$

It depends upon the variable E and e, the radius of the non-deformed drop r, the coefficient γ, and the ratio ε′/ε′′.

The deformation of the drop as a function of the eccentricity e in a given field intensity E can be determined from the condition of the minimum total energy (106):

$$\frac{\partial W(e,E)}{\partial e}=0$$

This is done be Gemant by approximate method of introducing two independent parameters

$$q=\frac{rE^2}{\gamma}\ \text{и}\ \alpha=\frac{c}{r}\cdot\frac{1}{\sqrt[3]{1-e^2}}.$$

and

The first of them depends only upon the field E, and the second depends upon the major axis of the ellipsoid of revolution and the radius of the sphere of the undeformed drop. The solution is found graphically or from the functional curves $\alpha=f_n\left(\frac{W}{2\pi r^2\gamma}\right)$

in various values of Q (from 3 to 10). Moreover, from $\frac{dW}{d\alpha} = 0$, Q is determined for $\alpha > 4$.

It should be noted that this theory neglects the interaction of polarized water ellipsoids, which would be permissible only in small concentrations of water drops. As breakdown criteria, the applied field intensity E is taken, in which the formation of a water bridge takes place. But the author of the theory considers that the condition of formation of such a bridge need not necessarily be the contact of polarized drops one from another, they may draw closer themselves under the action of coulomb forces. If this self-approximation is not considered, and it is considered that drops are joined in a dense bridge only under the action of an applied voltage, then the value of E_{br} would be strongly increased.

According to the derived formulas one can quantitatively determine E_{br} as a function of the degree of wetting of the isolated liquid. Gemant's theoretical curve of the dependence of E_{br} of transformer oil upon the concentration of water in it closely coincided with the experimental curve in Fig. 16.

The basic deficiency of this theory can be considered to be its sketchiness. In the basis of the breakdown mechanism, ionization processes, cold emission from the cathode, the influence of electrode material, the formation of volume charges, etc., do not figure at all. By Cohen's rule (L.88), suspended foreign particles with a large dielectric permeability are charged positively relative to the solvent with a decreased ε something similar should take place also with suspended drops of water in transformer oil. In the case of an applied voltage, the transmigration of charged drops and oil particles should therefore take place. This physical process is not taken into account in the theory either.

Concerning the close coincidence of experimental and calculated data, this, evidently, was possible mainly on account of the arbitrary selection of the quantity E, in which the process of the self-approximation of the polarized bubble of water should take place.

The sketchiness of Gemant's theory is somewhat corrected in the theory of Boeing (L.306 and 307), which although it is also tentative, it provides an answer to the problem of the sources of current bearers. According to the theory the same water drops from which the dense bridge are formed, serve as these sources. According to Boeing inside the drops there are ions in which the water molecules are dissociated. Part of these ions will be absorbed by the surface of the canal. The chemical nature of the liquid dielectric and its structure is considered only by the amount of ions which can be absorbed by the surface of the canal from the water drops.

When the voltage is turned on, from the motion of the ions inside the drop, the current goes along the canal. The ions absorbed by the surface of this canal will become almost motionless in small voltages. Their role is increased only in completely specified voltages. The current between the electrodes also sharply increases. The voltage in which this increase occurs, Boeing considers to be the breakdown voltage. In principle the same picture of breakdown formation, according to this theory, should be used also with alternating current, if during the time of the semi period, a distribution of the charges along the surface of the canal takes place. The greater the frequency, the greater E_{br} should also be. According to this theory there is a possible between U_{br} and the length of the spark gap l:

$$U_{br} = al + bl^2. \qquad (107)$$

For special cases we obtain from this formula

$$U_{br} = al \text{ and } U_{br} = bl^2. \qquad (108)$$

An example of the same dependence in certain liquids in specified conditions is also observed in experiment.

A connection can qualitatively be established between U_{br} and the wetness (formation of a bridge of water drops). However, the initial state of the theory is not compeletely evident. The dynamics of breakdown formation are not reflected in the theory either. A source of current bearers is assumed to exist, but is latent until a certain moment. Therefore there is no necessity of including the mechanism of impact ionization.

From the point of view of contemporary refinements on the developments of breakdown the mathematical interpretation of this phenomenon is inadequate. Meanwhile a convincing theory of breakdown of wet liquid dielectrics has still not been suggested.

CHAPTER NINE

A THEORY OF BREAKDOWN TAKING INTO ACCOUNT CHEMICAL TRANSFORMATIONS IN LIQUIDS, COLD EMISSIONS OF ELECTRONS, AND IMPACT IONIZATION

9-1. The Volt-ionization Theory

In Section 2-3 experimental data are presented on the separation of gas from transformer oil when a constant voltage is switched on. There it was noted that such gas separation takes place even in thoroughly de-gassed oil during a certain reduction in the outside pressure. The same thing takes place in liquid hydrocarbons during silent electrical discharges. The physical-chemical properties of liquids are changed: the temperature of flashover is increased, the specific weight in increased, etc. In specified applied field intensityies in hydrogen or nitrogen media with reduced pressure, in liquids luminous blue gas bubbles are formed (L.154). The separation of gas in the given case is a consequence of chemical transformation (voltolization). It is suggested that in an electric field with bombarding of molecules by ions of the gas medium and in the chemical interaction of liquids with different molecular weights, hydrogen is liberated. In the case of a large field intensity the same thing, apparently, may transpire with bombarding of molecules by electrons emitted from the cathode.

According to Florensky (L.308), the breakdown of liquid dielectric with non-de-gassed electrodes is formed right with the participation of the volt-ionization processes. In the electrodes gas bubbles are always present. The ionization processes begin in them at a certain voltage. From the ionic bombardment a destruction of the molecules of the liquid takes place and hydrogen is liberated. The volume of the bubble and its charge are increased. With the departure of negatively charged ions such bubbles are charged with the same charge from the electrodes. As a result of electrostatic repulsion, they break away from the electrode and migrate under the action of the electrical force $F = qE$ to the direction of the other electrode. Such a breakaway takes place in the case where this F is equal or greater than the force of the surface tension:

$$qE = 2\pi\gamma a; \qquad (109)$$

Here γ is the coefficient of surface tension;
a is the radius of the base of the bubble.

Reaching the opposite electrode and becoming neutralized, the bubbles will rise to the surface of the liquid. It is suggested that in the case of the breakaway there remains a certain quantity of gas which will serve as the embryo for the formation of a new bubble, etc. At a certain speed of these processes between the electrodes, finally a dense bridge is formed of such bubbles in which the breakdown is formed.

According to Vol'kenshtayn (L.309) such formation is possible in a condition

$$\Delta S = \theta r = v\Delta\tau \qquad (110)$$

where ΔS is the spacing between the centers of the two closest bubbles of the gas;
r is their radius;
θ is the condition constant;
$\Delta\tau$ is the time of breaking away of the bubbles;
v is the speed of their departure from the place of formation.

The velocity v according to Stokes, is equal to:

$$v = \frac{qE}{6\pi r\eta} \qquad (111)$$

where η is the viscosity. Then

$$\Delta S = \frac{qE\Delta\tau}{6\pi\eta r} \tag{112}$$

and

$$\frac{qE\Delta\tau}{\pi\eta r^2} = 6\theta. \tag{113}$$

From (109) and (113) we obtain:

$$\eta \frac{r^2}{\Delta\tau} = \frac{\gamma a}{3\theta} = A. \tag{114}$$

By convention, A may be taken as a constant.

At the surface of the bubble $S = 4\pi r^2$ equation (113) may present the following form:

$$\eta \frac{S}{\Delta\tau} = \frac{4\pi\gamma a}{3\theta} = B.$$

Let us designate then increment on the surface of the bubble for the time $\Delta\tau$ as $\Delta S = S - S_0 = S$,ΓπeS$_0$, where S_0 is the initial surface with radius a. If we neglect it, then:

$$\eta \frac{\Delta S}{\Delta\tau} = \text{const.} \tag{115}$$

Since, according to (113), $E_{br} = f(\eta \frac{\Delta S}{\Delta\tau})$, then the breakdown condition should be determined by the product of the viscosity and the velocity of the increment of the surface of the bubble or the speed of increase of the surface energy. It may be further assumed that

$$\frac{\Delta S}{\Delta\tau} = f\left(\frac{dn}{d\tau}\right).$$

where n is the number of gas molecules in a bubble, and the derivative $dn/d\tau$ should determine the speed of the process of voltolization, i.e., the speed of bubble formation, and consequently also molecules of hydrogen. However, the expanded form of this function is unknown; therefore the breakdown criterion of the voltolization mechanism can be formulated only qualitatively.

It is completely obvious that the formulation of breakdown in voltolization can take place only in the case of a prolonged applied voltage. From the formulas derived above, it follows that the speed of volotolization increases together with E. Therefore, the factors accelerating this process should decrease the quantity E_{br}.

From experiments it is known that the more complicated the hydrocarbon molecule in the homologous series, the more intensively the process of voltolization takes place; consequently, U_{br} should be reduced according to the degree of enlargement of the molecule of the liquid. This is as if it were confirmed in an experiment more than half a century ago (L.310). However, in later experimental data it turned out that the value E_{br} of the liquid hydrocarbons of the paraffin series in an increase of the specific weight increase (see Section 1-3 and Figs. 1 and 4). This regularity is established for very small spark gaps (several dozen microns). Data on the regularity of E_{br} upon the density for longer intervals and prolonged applied voltages do not yet exist.

From the point of view of the theory in question one can qualitatively establish also the influence of frequency of the applied voltage upon E_{br}. If the time $\Delta\tau$ in the course of which the bubble is formed and breaks away from the electrode, is greater than the half period in the alternating voltage, then the breakaway may not exist and the entire charge of the bubble in the alternating sign of the applied voltage migrates to this electrode. Consequently, in an increase of the frequency U_{br} should increase. In a frequency range of 50-500 Hz., this is significantly observed in breakdowns of transformer oil and hexane.

9-2. The Theory of Breakdown Taking into Account Cold Emissions of Electrons from the Cathode

The existence of cold emission of electrons from the cathode as was noted above, is shown by experimental means. The question arose on its influence upon the quantity E_{br} of liquids. The theory of Bragg, Sharbaugh, and Crowe (L.151) is devoted to this question. In the theory is considered only the pre-distribution of the applied voltage along the spark gap from the appearance of the volumetric negative charge. The acceleration of the electrons by the applied field and the impact ionization related to this is not taken into account in the theory. The diffusion of emitted electrons is also omitted.

In the formation of volumetric negative charge the voltage of the field at the cathode is decreased, but is increased in the remaining length of the inter-electrode gap. How great is this increase and is the formation of breakdown possible in places with the greatest voltage after pre-distribution, if the applied voltage is less than the breakdown voltage? This question in the theory under discussion, is basic.

For plane parallel electrodes of infinite area at a distance l, we may write:

$$\frac{d^2\varphi}{dx^2} = -\frac{4\pi\rho}{\varepsilon}; \quad J = -\rho k \frac{d\varphi}{dx} \text{ and } 0 \leqslant x \leqslant l; \tag{116}$$

in these conditions φ is the potential, ε is the dielectric permeability, ρ is the density of the volumetric charge, and k is the mobility of the charged particles. For simplifying the problem the positive ions are not taken into account.

In grounding one electrode, the boundary conditions will be the following:

$$\begin{array}{llll} \varphi & = 0 & \text{for} & x = 0; \\ \varphi & = \varphi_G & \text{for} & x = l; \\ -\frac{d\varphi}{dx} & = E_k & \text{for} & x = 0; \end{array} \qquad (117)$$

here E_k is the cathode voltage.

In the emission of electrons, we may assume for now that the field intensity in this place will be equal to 0 ($E_k \approx 0$). Then the solution of (116) gives:

$$\varphi = \varphi_0 \frac{x^{4/3}}{l^{4/3}}; \qquad (118)$$

$$\rho = -\frac{3\varepsilon\varphi_0}{16\pi l^{4/3} x^{2/3}}; \qquad (119)$$

$$J = \frac{9\varepsilon k \varphi_0^{3/2}}{32\pi l^2}. \qquad (120)$$

The voltage at the annode may be determined from (118):

$$E_a = -\left(\frac{d\varphi}{dx}\right)_{x-1} = -\frac{3}{2} \cdot \frac{0}{l} \quad . \qquad (121)$$

From (120) it follows that the current density does not depend upon x. Consequently, for X = 0 when $E_k = 0$ the current in the given boundary conditions will not be equal to 0. Since however, for $E_k = 0$ the current must necessarily be absent, then equation (116) should be solved in the supplementary boundary condition. If the current of cold emission exists, then for x = 0 the quantity $E_k \neq 0$. In this boundary condition, from the solution of (116), for the potential the following expression is obtained:

$$\varphi = \frac{\varepsilon k}{12\pi J}\left[\left(\frac{8\pi J x}{\varepsilon k} + E_k^2\right)^{3/2} - E_k^3\right]. \qquad (122)$$

If we set $E_k = 0$, then the equation coincides with (118).

Since according to (117) for $x = l$, the potential $\varphi = \varphi_0$, then from (122) we obtain:

$$\varphi_0 = \frac{\varepsilon k}{12\pi J}\left[\left(\frac{8\pi J l}{\varepsilon k} + E_k^2\right)^{3/2} - E_k^3\right]. \qquad (123)$$

For an analysis of the equations obtained, we may assume:

$$E_{cp} = \frac{\varphi}{l} \text{ (average field intensity);}$$

$$\gamma_k = \frac{E_k}{E_{cp}} = \frac{E_k l}{\varphi_0} \text{ (the reduced field intensity);}$$

$$\eta = \frac{8\pi l J}{\varepsilon k E_{cp}} = \frac{8\pi l^3 J}{\varepsilon k \varphi_0} \text{ (the reduced current density).}$$

then (123) takes on the following form:

$$\eta = \frac{2}{3}\left[(\eta + \gamma_k^2)^{3/2} - \gamma_k^3\right]. \qquad (124)$$

This equation determines the dependence between the reduced current density and the field intensity at the cathode.

The reduced voltage at the annode $\gamma_a = \frac{E_a}{E_{cp}}$ may be found from the differential of (122), since

$$E_a = -\left(\frac{d\varphi}{dx}\right)_{x=l}$$

In Table 51, the values of γ_a and η are presented for different γ_k. These relations are calculated from (124). Using these data, we may trace from the redistribution of voltage in the inter-electrode gap to the formation of breakdown. For example, in the case where the field intensity at the cathode is equal to 0, then at the anode it will be $\gamma = 1.5$, i.e., three halves larger than the average voltage. For $0 < \gamma_k < 1$ the field intensity at the annode will be greater than 1 ($\gamma_a > 1$). From the table it follows that for cold emission of electrons from the cathode the field intensity at the annode may be significantly larger than average.

TABLE 51

VALUES OF γ_k, η and γ_a

γ_k	0	0.20	0.40	0.60	0.80	1.0
η	2.25	2.14	1.84	1.35	0.70	0
γ_a	1.50	1.48	1.41	1.31	1.16	1.0

The current of electron emission is determined by the field intensity at the cathode; the same is also true for η:

$$\eta_k = \frac{J_k}{E_{cp}^2} \approx e^{-\frac{b}{\gamma_k E_{cp}}} . \qquad (125)$$

From the data of Table 51 and equation (125), for a qualitative view of the problem, in Fig. 117 a graph is constructed of the current η and the reduced voltage E_a at the anode in arbitrary units. Along the axis of the abcissas here is laid out the average voltage E_{cp}. From the graph it is evident that the current density increases exponentially along curve 2, if there is no volumetric charge; when there is a volumetric charge the current changes according to curve 1.

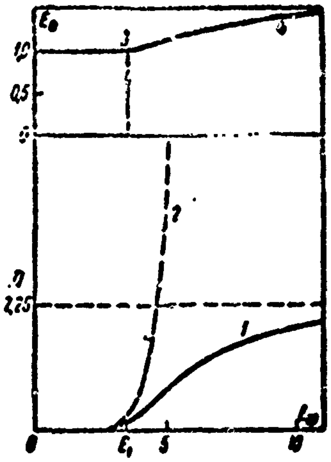


Fig. 117. Current as a function of field intensity at the annode and the average voltage of the applied field in arbitrary units.

1 - the actual current; 2 - the curve of current emission from the cathode; 3 - the current at the annode to the point E_1, 4 - the same, but with values $E_{cp} > E_1$

For small values of the average field intensity $E_{cp} = E_1$ the emission current is small and the field intensity at the annode does not yet change (point 3). For large values of E_{cp}, the emission of current increases and the current at the annode increases, but to a certain limit (curve 4). In the present arguments it is assumed that the mobility of the electrons does not depend upon the field intensity; consequently the possible capture of electrons by molecules is not considered.

For a different quantity of field intensity at the annode, the process of impact ionization may begin and also breakdown. Consequently, in the theory under discussion a description is given only of the pre-breakdown stage, when the necessary condition is created for such formation.

Let us assume that there are three cathode materials with different work values of electron removal. The current density of cold emission from these cathodes J as a function of the applied field intensity E is shown by Curves I, II, and III in Fig. 118. The dotted curve 1 presents the current density of emission which takes place in the actual conditions taking into account the influence of the negative volumetric charge.

in the case where the cold emission is significant only in voltages greater than E_i. But if this emission is comparatively large in voltages E_{cp} in a range of $2/3\ E_i - E_i$, then the influence of the cathode material may not be neglected.

According to Swan's theory (L.311), electron emission is also a decisive factor in the development of breakdown, but the increase in positive ions by the volumetric charges continues, which ions are accumulated at isolated or semi-isolated films on the cathode surface. Impact ionization in liquids in the formation of breakdown, although not rejected, is considered an indecisive factor. Such an emission is made on the basis of current measurements in n-hexane (see Fig. 99), in voltages close to the breakdown voltage (L.147 and 221). Swan writes the equation for electron emission from the cathode in the following form:

$$J_c = A\mu^2 E_c e^{-B\ell\mu E_c}, \tag{126}$$

where J_c is the density of electron current;

E_c is the actual field intensity in the presence of distortion;

μ is the coefficient of local field strength;

A and B are constants, depending upon the surface of the cathode.

It is assumed that μ does not depend upon field intensity. If the field from the positive ions is designated as E_+, then

$$E_c = E_0 + E_+; \tag{127}$$

when there is no volumetric charge, $E_c = E_0$.

From (196) and (127), we obtain:

$$J_c = J_0 \left(1 + \frac{2E_+}{E_0}\right) e^{BE} + \ell\mu E_0^3 . \tag{128}$$

In the presence of charged particles between electrodes, Leb (L.271) derived a formula for the field intensity E for the distance x from the cathode:

$$\frac{d}{dx}(E^2)=\frac{8\pi J_c}{\varepsilon}\left[\frac{1}{k_+}\exp\left(\int_0^l \alpha dx\right)-\left(\frac{1}{k_+}+\frac{1}{k_-}\right)\exp\left(\int_0^x \alpha dx\right)\right], \tag{129}$$

where a is the coefficient of ionization for voltage E;

k_+ and k_- are the mobility of the charged particles;

l is the spacing between electrodes;

ε is the dielectric permeability of the medium (liquid).

If the field distortion by the volumetric charges is not large throughout the inter-electron space, then E may be changed to $E_0 + \Delta E$ $(\Delta E < E_0)$.

In the integration of equation (129), the coefficient α is taken as independent of the field $\alpha = \alpha_0$. After integration and substituting $E^2 = E_0^2 + 2E_0\Delta E$, the following equation is obtained:

$$\Delta E=\frac{1}{2\varepsilon E_0}\left\{C-\varepsilon E_0^2-8\pi J_c\left[\frac{x}{k_+}e^{\alpha_0 l}-\left(\frac{1}{k_+}+\frac{1}{k_-}\right)\frac{e^{\alpha_0 x}}{\alpha_0}\right]\right\}. \tag{130}$$

The integration constant C is determined from

$$\int_0^l \Delta E\, dx = 0.$$

The field distortion E_+ may be determined from (130) setting $x = 0$:

$$E_+ = GJ_C , \tag{131}$$

where

$$G=\frac{4\pi l}{\varepsilon k_+ E_0}\left\{\frac{1}{2}e^{\alpha_0 l}-\left(\frac{1}{k_+}+\frac{1}{k_-}\right)\frac{k_+}{\alpha_0^2 l^2}\left[e^{\alpha_0 l}-\alpha_0 l-1\right]\right\}. \tag{132}$$

In a small intensity of impact ionization, when $\alpha_0 l$ is small,

(132) is simplified:

$$G = \frac{2\pi l}{\varepsilon k_+ E_0} \left(\alpha_0 l - \frac{k_+}{k_-}\right). \qquad (133)$$

From (133) it follows that the sign of field distortion is determined by the quantities $\alpha_0 l$ and k_+/k_-. It is known from experiments that ion mobilities in liquid dielectrics are not the same, and the ratio k_+/k_- should therefore characterize the liquid. For example, for $E<1$ kv/cm, according to (L.212), for n-hexane k_+/k_- 0.308 the mobility of negative ions does not depend upon the field to 500 kv/cm (L.313). But in higher voltages according to the data of (L.158), it evidently is significantly increased. In liquid argon, according to (L.134), electrons remain free even in the case of very small E, and for 100 kv/cm, the ratio k_+/k_- is equal to 10^{-4}.

If the value of k_+/k_- may be neglected in comparison to $\alpha_0 l$, then

$$G = \frac{2\pi j_0 l^2}{\varepsilon k_+ E_0}. \qquad (134)$$

According to the data of (L.314), for argon

$$j_0 = C_0 \exp\left(\frac{D}{E^{1/4}}\right). \qquad (135)$$

Substituting (135) in (134) and calculating (131) for the field intensity at the cathode, we obtain the expression:

$$E_c = E_0 + \frac{2\pi l_c C_0 l^2}{\varepsilon k_+ E_0} \exp\left(-\frac{D}{E_0^{1/4}}\right). \qquad (136)$$

If we now construct a graph in which the axis of the ordinate gives the density of cathode current (126) and the abscissa axis gives the field intensity E_c (136), then for certain (arbitrary) values E_0 (1.15 mv/cm), ε, k, μ, l, A, B, C, and D, two curves are obtained intersecting in two different points. One point of intersection Swan considers to have no physical meaning, and the second fits the established regime when this change of G_c is absent. For two other arbitrary values of E_0 (1.24 and 1.4 mv/cm) the curves do not intersect. The author of the theory considers this characteristic of the non-established regime, in which the positive ions at the cathode continually induce emission current to the breakdown of the liquid.

For E_{br} the value of E_c is taken in which two curves are tangent. Although a stationary regime is established the small value of E_0 gives rise to a continuous current increase J_c. In the corresponding selection of the value of B in (126) the calculated dependence curve $E_{br} = f(l)$ for liquid argon closely coincides with the experimental curve.

9-3: Theories Taking into Account Cold Electron Emissions and Impact Ionization

An attempt to develop a theory of the breakdown of liquids taking into account cold electron emission from the cathode and impact ionization is done by Goodwin and McFadden (L.91). The effect of impact ionization is also considered in the equation of Loeb (129) but in assuming that the ionization coefficient α throughout the points of the inter-electrode gap are the same. Since, however $\alpha = f(E)$, then this is equivalent to assuming the absence of an induced field in the inter-electrode space from electrons of cold emission. In the foregoing paragraph it was already shown that this does not correspond to reality. The unconvincingness of the basic premises is comprised mainly in the fact that the influence of cold emission upon E_{br} is sought for, however, in one significant assumption this influence is neglected.

The current density of cold emission in any point of the gap between the electrodes of length l at a separation x from the cathode is equal to $J_- = J_0 e^{\alpha x}$ and at the annode $J_- = J_0 c^{\alpha l}$. According to their condition of continuity, the overall current should consist of the sum of the currents $J = J_- + J_+$, (L.271 , page 345). But inasmuch as there is no positive ion emission from the annode, the total annode current is

$$J = J_0 e^{\alpha l} = J_0 e^{\alpha x} + J_+, \tag{137}$$

whence
$$J_+ = J_0 \left(e^{\alpha l} - e^{\alpha x}\right).$$

The influence of the sxtended charge for the homogenous case may be determined by Poisson's equation:

$$\frac{dE}{dx} = -\frac{4\pi}{\varepsilon}\left(q_+ - q_-\right). \tag{138}$$

for the velocity of charged particles v, the current J = qv and v = kE, where k is the mobility. Therefore, J = qkE.

Inserting the value $q = \frac{J}{kE}$ in (138), we obtain:

$$\frac{d(E^2)}{dx} = -\frac{8\pi J_0}{\varepsilon}\left(\frac{e^{\alpha l} - e^{\alpha x}}{k_+} - \frac{e^{\alpha x}}{k_-}\right). \tag{139}$$

The diffusion of charged particles and electron capture by molecules is not taken into account. The integration of (139) for α = const yields:

$$E = \frac{8\pi J_0}{\varepsilon}\left[\frac{x e^{\alpha l}}{k_+} - \left(\frac{1}{k_+} + \frac{1}{k_-}\right)\frac{e^{\alpha x}}{\alpha}\right] + E_0^2, \tag{140}$$

where E_0 is a constant which should be determined from the boundary conditions:

$$\int E\,dx = E_a l; \tag{141}$$

here E is the field intensity at a distance x from the cathode; E_n is the applied voltage.

The authors determine E_0^2 by the integration of both members of the equation (140) from 0 to l, and obtained:

$$E_0^2 = E_n^2 + 2\left[\frac{2\pi J_K l e^{\alpha l}}{k_+} - 8\pi J_K\left(\frac{1}{k_+} + \frac{1}{k_-}\right)\frac{e^{\alpha l}}{2\alpha^2 l}\right]. \qquad (142)$$

For a field intensity close to the breakdown intensity $(E_n \; E_{br})$ the second member in brackets may be neglected relative to the first.

The voltage at the cathode is found from (140) by plugging into it the value of E_0 from (142) and for x = 0:

$$E_K = E_n + \frac{2\pi J_K e^{\alpha l}}{k_+ E_n}. \qquad (143)$$

If the index function in the equation of Fowler and Nordheim (22) is expanded into the series and restricted to the first two members, then $J_k \; aE_k^2(1-\frac{b}{E_k})$. After inserting this expression in (243), the relation can be established between E_k and E_n:

$$E_K - E_n \approx \frac{CE_K^2 - bCE_K}{E_n}, \qquad (144)$$

where

$$C = \frac{2\pi a l e^{\alpha l}}{k_+}.$$

For determination of the breakdown voltage the authors used the equation of Fowler and Nordheim and (143). In each of them the emission current of the electrons J_k and the field intensity at the cathode E_k is figured. But in (143) the applied voltage E_n enters. For given values of E_n, it is possible from the two equations to graphically determine J_k and E_k. Such a qualitative determination is performed in the graph of Fig. 119. The curve constructed according to the equation of Fowler and Nordheim is designated OB. From (143) it is evident, that for values of E_n the dependence between J_k and E_k is linear. It is represented by the lines PQ. The point P_1 on the abscissa's axis signifies that for a given E_k and E_n' the emission current is equal to 0. P_2Q_2 and P_3Q_3 represent the function $J_k = f(E_k)$ for higher values of E_n. The curve OB and P_3Q_3 do not intersect for a certain E_n', but do have a point of tangency. For voltages somewhat larger than E_n', the equilibrium state in the inter-electrode gap is destroyed, and a condition is created suitable for breakdown formation. Therefore the authors of the theory consider $E_n = E_{br}$. Principally this same criterion for determining the breakdown voltage was used also by Swan (L.311).

It was noted above that generally on the surface of electrodes emersed in a liquid, there are isolated or semi-isolated films which exert a strong influence on electron emission, and the equation of Fowler and Nordheim is not applicable here. Therefore the breakdown criterion of Goodwin and McFadden must be considered an insufficient basis.

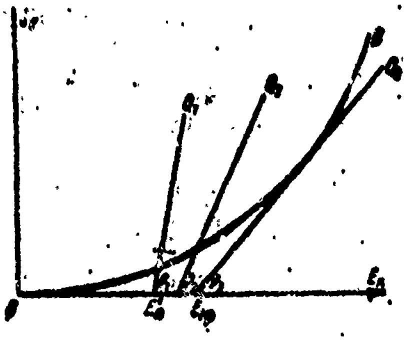


Fig. 119. Conditions for breakdown of liquids for cold cathode electron emission.

CHAPTER TEN

OTHER THEORIES OF BREAKDOWN

10-1. A Theory of Breakdown Taking into Account the Polarization of Solid and Liquid Additives

The formation of bridges by polarized impurities in a prolonged applied voltage is taken as the basis for the construction of the breakdown theory of Cook and Corby (L.315-317). If the dielectric permeability ε of the foreign particles is larger than that of the liquid, then they should migrate to the place with the highest voltage where the breakdown bridge will also be formed. The possibility of impact ionization is allowed in them. A large field intensity may be at the edge of the electrodes, at the predicting edge and at various kinds of projections. The foreign particles are polarized and acquire a moment m, proportional to E.

The authors examine a rectilinear system of coordinates with a center in a spherical grid of particles whose dielectric permeability constant is ε. This element is in the dielectric medium ε_0. The condition is examined where $\varepsilon > \varepsilon_0$. The force acting on the polarized spherical particles, as is known from electrodynamics is equal to:

$$f_1 = r^3 \frac{\varepsilon - \varepsilon_0}{\varepsilon + 2\varepsilon_0} E \,\mathrm{grad}\, E; \qquad (145)$$

it does not change sign in the course of the entire period of the applied alternating voltage.

For simplyfing the problem it is assumed that: $\varepsilon \to \infty$ and $E = \frac{dE}{dx}$ (homogeneous condition) then

$$f_1 = r^3 E \frac{dE}{dx}. \qquad (146)$$

For the motion of charged particles in an inhomogeneous field they will experience a deceleration, the force of which in a medium with a viscosity η, according to Stoke's law is equal to:

$$f_2 = 6\pi\eta r v_0(x). \tag{147}$$

From equations f_1 and f_2, the velocity is determined

$$v_0(x) = \frac{r^2}{6\pi\eta} E(x) \frac{dE(x)}{dx}. \tag{148}$$

Since the particles are collected in the places with the highest voltage, their concentration there should be greater than in the neighboring areas. Diffusion motion arises in the place with less concentration. It is assumed that the velocity of the particles in the electric field may become equal to the diffusion velocity v_1 for the motion of particles in negative voltage:

$$v_1(x) = -\frac{D}{N(x)} \frac{dN(x)}{dx}, \tag{149}$$

where D is the diffusion coefficient;

N is the quantity of foreign particles per cm^3. According to the Stoke's-Einstein formula,

$$D = \frac{kT}{6\pi r\eta}$$

and

$$v_1(x) = \frac{kT}{6\pi r\eta N(x)} \frac{dN(x)}{dx}. \tag{150}$$

Setting $v_0 = v_1$, we may obtain an expression for the critical field intensity E(x), above which sooner or later the breakdown should form.

In using the barometric function for a concentration N(x) in the given equilibrium state, the following dependence is obtained of the breakdown voltage upon the radius r of the polarized particles:

$$r^3E^2_{\text{пр}} = \frac{1}{4}kT, \qquad (151)$$

and for the breakdown delay time τ_B:

$$\tau_{\text{в}}^{1/2}g^2r^3\left(E^2_{\text{пр}} - E_0^2\right)N = \text{const.} \qquad (152)$$

In this formula g characterizes the degree of inhomogeneity of the field; E_0 is the breakdown voltage for a prolonged applied voltage.

For short pulses E_{br} of extremely pure hydrocarbon liquids, as was already noted, is equal to 1.4 - 1.5 mv/cm. The corresponding molecular diameter, according to (151), then should be equal to approximately 14Å. Actually in liquid hydrocarbons with the specified E_{br} these diameters are significantly smaller. Therefore the authors of the theory suggest that the breakdown is formed in places with a predominance of polymerized or oxidized molecules, the diameters of which are larger than normal.

In connection with the aforementioned theory it should be noted that there is still not enough experimental material to evaluate its applicability. Certain of the assumptions in deriving the equations do not seem well-founded. For example, the authors assume that $\varepsilon = \infty$. This, generally speaking, would be suitable only for metallic impurities. The authors attempt to extend the derived formulas to the breakdown of very pure hydrocarbon liquids, in which the polarized particles responsible for the breakdown are considered to be oxidized hycrocarbon molecules. It is entirely clear that ε of the oxidized liquid will not be significantly different from ε_1 of the unoxidated liquid and in any case will not be too large.

It is not understandable that the velocity of the polarized particles moving in the electrical field should be equated to the velocity of the diffusion motion of these particles. Such a condition may be an equilibrium without motion but then it is not necessary to speak of velocities. Moreover, the formula for the diffusion of particles assumes that they move randomly. The equation (151) is introduced for polarized particles under the action of an applied electrical field.

10-2. A theory on the basis of the concept of impact ionization and the interaction of electrons with the molecules of the medium

In the theory of Lewis stated below (L.24, 90, and 318) although it does not reject the influence of emission as a source of electrons the distortion of the field due to it in comparison with other factors is considered small and is therefore not taken into account. The capture of electron avalanches by the molecules of the liquid is also rejected. Such a simplification of the method due to the complexity of the breakdown process seems, of course, unnecessary.

In this theory a great deal of attention is devoted to the interaction of electrons with molecules of the medium according to Hippel (L.25). The electrons in drifting in the direction of the field, as was noted earlier, received energy from the applied fie and expended it in the excited vibrations of the particles of the medium. In small intensities the electrons have a small energy and in the quantum interaction with particles of the medium cannot give them small portions of energy. The same thing happens with electrons having large velocities due to the smallness of the time of interaction in the course of which the vibration of the particle is not disturbed. Consequently there should appear an optimum E or an optimum energy of the electron W, in which they most effectively give up their energy to the molecules of the liquid.

If an argument is introduced relative to the average length of the free electron path λ, then the energy may be written:

$$W = Ee\lambda = \frac{mv^2}{2} = h\nu. \qquad (153)$$

theory, have the same corresponding frequency of vibration ν_0. This assumption is made on the basis of spectrographic data on the frequency of vibrations of certain hydrocarbon groups (L.319). Generalizing these data, Lewis made the not entirely strict assumption that the vibrational barrier is the same for all hydrocarbon liquids. This, of course, need not signify that they must all have the same E_{br}, since the length of the free path λ is different.

The average length of the free path λ is determined from the amount of the capture cross section Q_i, where i = 1,2,3 - are the indexes corresponding to the group CH, CH_2, and CH_3:

$$\lambda = (\Sigma Q_i N_i)^{-1}. \tag{155}$$

The tentative calculation of O_i may be made on the assumption that the enumerated groups of atoms are distributed along the spherical surface. As the radius of the sphere, the distance 1.1Å may be taken between the atoms C and H and in the C-H bond. In this section Q $3.8 \cdot 10^{-16}$ cm^2. It can be determined more exactly starting from the assumption that the shape of the molecule is cylindrical, and calculating at not a transverse but a lengthwise section of the cylinder of radius r and length l.

In the work (L.320) as the radius, the half distance between the axes of the molecule $2r \approx 4.9$Å, was taken, and for l, the length of the C-C bond projected along the axis of the cylinder (l = 1.23 Å). For a number of hydrocarbon atoms n

$$Q = 2rl(n-1) \text{ и } \lambda = [Nrl(n-1)]^{-1}.$$

Close to this theory of the breakdown of liquid dielectrics (see Section 1-3) is the theory presented in (L.21).

According to (154) and (155) the breakdown voltage was

In field intensities E_1 and E_2 this energy will be equal to W_1 and W_2. Its increment $\Delta W = W_2 - W_1$ is presented in Fig. 120 along the axis of the ordinate in the form of a straight line 1.

The energy losses by the electrons are presented in curve 2 with a maximum at the point W_0. In the area AB the losses predominate and the acceleration of the electrons does not take place (vibrational barrier) and consequently the process of impact ionization is little likely. Only in energies greater than B may this barrier be exceeded. In Fig. 120, besides the energy W_0, the ionization potential Φ may also be noted, the quantity of which may be distributed inside the area AB. This point is taken as a criterion of breakdown in the work (L.232).

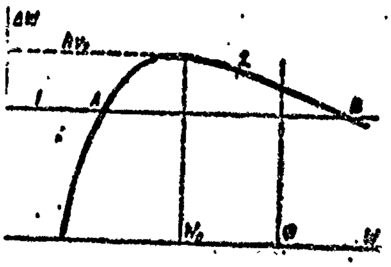


Fig. 120. The change in energy of the electrons moving in an electrical field, in the average length of the free path:

1 - the energy obtained by the electrons from the applied field; 2 - the losses in energy by the electrons to the excitation vibrations

For a certain simplification it may be considered that the molecules have a particular vibration frequency ν_0. It is assumed that in an induced force the alternating frequency is possible as if a resonance with the greatest absorption energy in the point W_0. According to (153) this should take place in a field intensity

$$E_0 = \frac{h\nu_0}{e\lambda}, \qquad (154)$$

which Lewis calculates from E_{br}.

But the greatest absorption is related not to the entire hydrocarbon molecule but to the separate groups it possesses CH, CH_2, and CH_3 which according to the assumption of the author's calculated for several liquid dielectrics and compared with experimental data (Table 52).

Table 52

Experimental and calculated quantities of E_{br} for several liquid hydrocarbons

Liquid hydrocarbons	E_{br} mv/cm	
	Experimental data	Theoretical data
n-pentane	1.00	1.07
3Me-pentane	1.03	1.06
n-hexane	1.10	1.18
3Me-hexane	1.05	1.12
n-heptane	1.20	1.23
2Me-heptane	1.21	1.18
3Me-octane	1.20	1.19
n-octane	1.30	1.39

From the table it is evident that the calculated and experimental values of E_{br} coincide very closely.

10-3. A theory of breakdown on the basis of the concept of the electrical density of the crystal dielectric

Atwood and Bixby (L.321) made a successful attempt to determine the breakdown voltage of carbon tetra chloride according to a formula derived for crystal dielectrics by Froehlich (L.294) and also Eiger and Teller (L.322 and 323).

The theory of Froehlich is based, as is known, on the assumption of Hippel on the interaction of the accelerated electrons in the applied field with the molecules of the medium (L.25). Moreover, it is postulated that the electrons in the zone of conductivity fall either by the tunnel mechanism or from "dumping" as a consequence of their distributed energy according to the law of Maxwell. According to Froelich, even at the beginning of the applied voltage the electrons have an energy sufficient for ionization by impact. In the absence of a field an equilibrium state of ionization and recombination is established in the dielectric.

At the base of the theory of Ziegger and Keller is placed the method of Boer for calculating energy lost by α-particles or going through the gas (L.324). The basic mechanism in this theory is impact ionization and the same assumption of Hiller on the interaction of electrons with the molecules of the medium.

For $U = U_{br}$ the electrons received from the applied field a high energy which they lose in the excitation of the vibrations of the ions of the crystal lattice. There is no impediment to the increase in the energy of these electrons. The impact ionization, the formation of an avalanche, and breakdown of the dielectric should come in very quickly. It is postulated that all the electrons accelerated by the field move directly without diffusion as α-particles in air.

For the calculation of Atwood and Bixby, the formula of Froelich was used in the following form:

$$E_{\text{пр}} = \frac{\pi^{2} e (m\hbar)^{1/2} (\varepsilon - \varepsilon_1) \nu^{3/2}}{8^{1/2} a_m \Phi} \left(\log \frac{4\sqrt{\Phi E_0}}{h\nu}\right)^{1/2} \times$$
$$\times \left(\frac{2}{e^{h\nu/kT} - 1} + 1\right)^{1/2} [\text{CGSE}]. \qquad (156)$$

The caculation of E_{br} is ocncucted in the following values of the separate parameters in (156): the average distribution between the molecules of CCl_4 $a_m = 4.45 \cdot 10^{-8}$ cm; the ionization potential $\Phi = \frac{hc}{\lambda_0}$ 5.42 ev, where λ_0 is the limiting wavelength of the absorption band; the dielectric permeability (the square of the index of refraction) $\varepsilon = 2.086$ and $\varepsilon_1 = 2.23$ (for long waves);

$$E_0 = \frac{2^{1/2}h^2}{32 m a_m^2} \approx 0{,}794\ \text{эв};\quad \log\frac{4\sqrt{\Phi E_0}}{h\nu} \approx 2{,}12$$

and

$$\left(\frac{2}{e^{h\nu/kT}-1}+1\right)^{1/2} = 1{,}025 \qquad T = 300^\circ\,\text{K}.$$

The calculated value of $E_{br} = 0.198$ mv/cm and the experimental value (in constant voltage) is $E_{br} = 0.66$ mv/cm.

According to the formula of Ziegger and Teller,

$$E_{\text{пр}} = \frac{1{,}83h^2 e m \nu}{h}\left(\frac{1}{\varepsilon_1}-\frac{1}{\varepsilon}\right)\left(\frac{\varepsilon}{\varepsilon_1}\right)^{1/2} \text{[CGSE]} \tag{157}$$

the value of the breakdown voltage of CCl_4 obtained was somewhat greater (0.26 mv/cm). In this formula, e is the elementary charge; $m = 9.03 \cdot .0^{-28}$ g; h is Planck's constant; ν is the vibration frequency in the atoms in the molecules absorbing the energy of the electrons; ε is the dielectric permeability for long waves (the statistical value ε); ε is the square of the index of refraction for short waves.

In both cases the coincidence of calculated and experimental values of E_{br} which was obtained was satisfactory. In the experiments, no great difference in the values of E_{br} was found for chemically pure and commercial CCl_4.

On the basis of the foregoing, the conclusion may be made that a transference of the regularity of the breakdown formation of crystal dielectrics at least to CCl_4, is possible even in the range of temperatures far from the crystallization point (L.325). But it is still too early to say that there is a regularity for other liquid dielectrics.

the index of refraction) $\varepsilon = 2.086$ and $\varepsilon_1 = 2.23$ (for long waves);

$$E_0 = \frac{2^{4/3}\hbar^2}{32ma_m^2} \approx 0{,}794 \text{ эв}; \quad \log\frac{4\sqrt{\Phi E_0}}{h\nu} \approx 2{,}12$$

and

$$\left(\frac{2}{e^{h\nu/kT}-1}+1\right)^{1/2} = 1{,}025 \qquad T = 300^\circ \text{K}.$$

The calculated value of $E_{br} = 0.198$ mv/cm and the experimental value (in constant voltage) is $E_{br} = 0.66$ mv/cm.

According to the formula of Ziegger and Teller,

$$E_{пр} = \frac{1{,}82\pi^2 em\nu}{h}\left(\frac{1}{\varepsilon_1}-\frac{1}{\varepsilon}\right)\left(\frac{\varepsilon}{\varepsilon_1}\right)^{1/2} \text{[CGSE]} \tag{157}$$

the value of the breakdown voltage of CCl_4 obtained was somewhat greater (0.26 mv/cm). In this formula, e is the elementary charge; m = 9.03 · .0^{-28} g; h is Planck's constant; ν is the vibration frequency in the atoms in the molecules absorbing the energy of the electrons; ε is the dielectric permeability for long waves (the statistical value ε); ε is the square of the index of refraction for short waves.

In both cases the coincidence of calculated and experimental values of E_{br} which was obtained was satisfactory. In the experiments, no great difference in the values of E_{br} was found for chemically pure and commercial CCl_4.

On the basis of the foregoing, the conclusion may be made that a transference of the regularity of the breakdown formation of crystal dielectrics at least to CCl_4, is possible even in the range of temperatures far from the crystallization point (L.325). But it is still too early to say that there is a regularity for other liquid dielectrics.

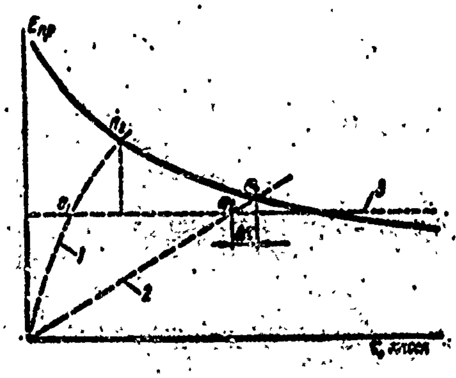


Fig. 121. A sketch to determine the time of breakdown delay. 1 - a sharp pulse; 2 - a slowly increasing pulse; 3 - E_{br} for constant voltage.

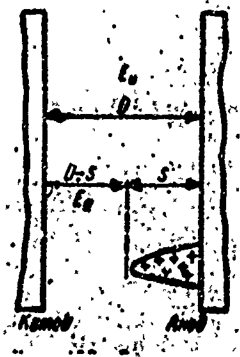


Fig. 122. A sketch for determining the time of breakdown delay of CCl_4 in pulsed voltage.

In work (L.321) the calculation is also presented of the delay time of breakdown formation in pulsed voltage. This time $\Delta\tau$ (Fig. 121) is determined as the interval between the moment when the amplitude of the wave front of the pulse 1 and 2 features a value equal to the breakdown value in constant voltage 3 (the points a_1 and a_2), to the moment of the beginning of breakdown in the points a_3 and a_4 in the pulses. Here Atwood and Bixby depart from the analogy with the mechanism of breakdown in gasses.

Let us assume that at the anode as a result of impact ionization, the formation of a positive volumetric charge has begun. For a certain moment of time the length of the area occupied by these charges is designated S for a distance between the electrodes D (Fig. 122). Let us designate the applied field intensity E_a, and the actual intensity between the cathode and the increasing positive streamer as E_d. If the streamer S is considered to be a good conductor, then from Fig. 122 the following equation is evident:

$$E_д(D-S)=E_а D. \qquad (158)$$

The quantity E_a may by Fig. 123 be changed by the breakdown intensity in constant voltage E_∞:

$$E_a = E_\infty + \tau \operatorname{tg} \alpha. \tag{159}$$

Since the speed of the growth of the streamer S is proportional to E_a, we may set

$$\frac{dS}{d\tau} = CE_a, \tag{160}$$

where C is a constant.

After substituting E_d from (158) and E_a from (159) and (160) we obtain:

$$\left.\begin{aligned} \frac{dS}{d\tau} &= C\frac{DE_a}{D-S} = \frac{CD}{D-S}(E_\infty + \tau \operatorname{tg} \alpha); \\ (D-S)\,dS &= CD(E_\infty + \tau \operatorname{tg} \alpha)\,d\tau; \end{aligned}\right\} \tag{161}$$

$$\left.\begin{aligned} \int_{S=0}^{D} (D-S)\,dS &= CD\int_{\tau=0}^{\Delta\tau}(E_\infty + \tau \operatorname{tg} \alpha)\,d\tau; \\ \frac{D^2}{2} &= CD\left(E_\infty + \frac{\Delta\tau \operatorname{tg} \alpha}{2}\right)\Delta\tau = \frac{CD}{2}(E_\infty + E_b)\,\Delta\tau; \end{aligned}\right\} \tag{162}$$

Here E_b is the breakdown voltage for pulse voltage.

Thus, if it is considered that the development of breakdown in liquids takes place in the same way as in gasses, by means of the motion of the positive streamer to the cathode, then the delay in the formation of breakdown $\Delta\tau$ should be inversely proportional to the average value from the breakdown voltage in the pulsed and constant voltages. For CCl_4 with $E_b = E_\infty = 0.66$ mv/cm the quantity $\Delta\tau$ 2.3 microseconds. The value obtained does not exceed a reasonable limit.

10-4. Statistical Theory

Based on the data of an experiment of the time of statistical lag of breakdown in liquid hydrocarbons of the paraffin series in short pulses and interelectron distances of several dozens microns, Lewis and Burg (L.326) proposed a statistical theory of breakdown. It is based upon an expression for the probability for the breakdown phenomemon $P(\tau)$ after the time τ from the beginning of the applied voltage and increasing it by degrees.

For breakdown in the interval τ and $d\tau$ this probability is written in the following form:

$$P(\tau) - P(\tau + d\tau) = f(E)\exp[-f(E)(\tau - \tau_f)]\,d\tau.$$

here E is the applied voltage; $\frac{1}{f(B)}$ is equal to the average statistical delay time, and τ_f is the time of breakdown formation.

For the average breakdown delay the expression is also obtained:

$$E_{sp} = E_0 + \int_{E_0}^{\infty} \exp\left[-\lambda \int_{E_0} \beta E\,dE\right] dE.$$

where E_0 is the threshhold field intensity, below which (E) is equal to 0, i.e., there is no breakdown , and for $B > E_0$ the value of $f(B)$ is quickly increases; λ is the number of rectilinear pulses with a given amplitude in one degree.

The value of P is determined from the expression

$$P = 1 - \exp[-f(E)(T - \tau_f)],$$

if the length of the square pulse is equal to P.

For short pulses and small intervals between the electrodes the calculated values of E_{br} and the experimental values coincide safisfactorily.

It is completely obvious that this theory may be applied to relatively large spark gaps. In these conditions the physical-chemical properties of the liquids and their structure will play the determining role.

10-5. Several Conclusions on the Theories of Breakdown in Liquids

On the basis of numerous investigations it may be considered established that the mechanism of breakdown of liquid dielectrics without impurities and additives includes three basic pcocesses

1) electron emission from the cathode;
2) impact ionization;
3) the interaction of electrons with particles of the medium.

In Chapters VIII-X it was shown that the incorporation of all these processes in one theory is not yet possible.

Secondary factors also participate in the formation of breakdown of technically isolated liquids besides the processes considered above. In several theories, (Gemant, Boening, , Cook, and Corby) attempts are made to consider them on the assumption that they play a decisive part in the breakdown. There are theories which are basically of a phenomenological character. A physical picture of breakdown formation is hardly touched upon in them.

Table 53

Basic Assumptions of Theories of Breakdown in Liquids

Name of Theory	Author of Theory	Basic Assumptions of the Theory	References
Gas	Gemant	Breakdown is formed in strongly deformed gas bubbles. Electrodes and the liquid serve as gas sources.	(L.299 and 300)
Gas-thermal	Edler	Breakdown formation takes place in a gas layer separating the electrode from the liquid. On the border of the separation of the liquid and the gas the temperature is increased and the liquid boils.	(L.301)
Thermal	Semenov and Walter	In the interelectrode gap, the temperature is highly raised. The breakdown is formed in the boiling liquid.	(L.302)
The same	Sharbo and Bivens	The breakdown in pulsed voltage may develop in gas bubbles, occuring from local heating and boiling of the liquid.	(L.303)
The same	Guntrschultz	The breakdown is formed along a gas path formed in the action of ions in the electric field.	(L.304 and 305)
Theory of a Droplet Bridge	Gemant	The breakdown is formed along a bridge(not necessarily dense) of polarized and highly deformed water droplets.	(L.75)
The same	Boening	Between the electrodes a bridge of water droplets is formed dissociating into ions which are fixed to the surface of this bridge with E_{br} these ions migrate and the bridge becomes a good conductor: the liquid breaks down.	(L.306 and 307)
Voltolization	Florenskiy, Wolkenstein	As a consequence of chemical action in the liquid	(L.308 and 309)

Continued

Name of Theory	Author of Theory	Basic Assumptions of the Theory	References
		hydrocarbons, gas bubbles are formed which form a dense bridge between the electrodes. The development of breakdown is due to the mechanism of impact ionization in this bridge.	
The Theory of Emission of Electrons from the Cathode	Bragg, Crowe, Sharbaugh	The electrons of cold emission form volumetric charge, which induces a redistribution of field intensity in the interelectrode gap. Breakdown formation begins in the places with the greatest voltage, equal to E_{br}.	(L.15)
Theory of Intensifying Emission of Electrons from the Cathode	Swan	Cold emission of electrons is increased by the field of positive ions captured at the semi-conducting film on the surface of the cathode. A redistribution of field intensity takes place and in the places with the voltage equal to E_{br}, breakdown begins to develop.	(L.311)
Theory of Emission of Electrons and Impact Ionization	Goodwin, and McFadden	Electrons of cold emission from the cathode produce impact ionization. Volumetric charge increases emission and breakdown progressively develops.	(L.91)
Theory of a Bridge of Polarized Impurity Particles	Cook, Corby	Formation of breakdown takes place along the conductive bridge of foreign particles polarized by the electric field, migrating to the places of highest voltage.	(L.315 and 317)

Continued

Name of Theory	Author of Theory	Basic Assumptions of the Theory	References
Theory of Impact Ionization and Interaction of Electrons with Particles of the Medium	Lewis	Breakdown progressively develops if electrons received more energy from the applied field than they lose in the action of oscillations of groups of atoms in the molecules of the liquid.	(L.24, 90, 318)
Theory Analogous to the Breakdown of Crystals	Atwood, Bixby	The development of breakdown is due to the mechanism of impact ionization if the free electrons already existing in the liquid or falling in the zone of conductivity due to the tunnel effect, receive from the applied field more energy than they lose in the disturbance of vibrations of particles of the medium.	(L.321)
Statistical	Lewis, Ward	Statistical factors are calculated in relation to the delay time of the breakdown.	(L.26)

Lewis' theory may be considered the simplest and most successful at the present time, in spite of the fact that it considers only impact ionization and the interaction of electrons with particles of the medium. A successful of breakdown in liquid dielectrics with additives and impurities has not yet been developed. In Table 53 the brief characteristics of breakdown theories, presented by various authors, are presented.

Conclusion

In the recent past comparatively simple methods have been used in the study of liquid dielectrics. In separate cases the non-coincidence of various experimental data was noted. This may be explained by the different treatment of studies of liquids and the insufficient control of the form of the wave of the voltage. Oscillograms were rarely used then, and the initial moment of breakdown remained unknown. It was assumed that it coincided with the time that the amplititude of the impulse reached the greatest value. Only long afterwards did it appear that the liquids break down with a great delay and that later with an increase in the distance between the electrodes it increases.

A wider introduction of high voltage cathode oscillographs in experimental research with liquids made it possible to obtain concepts on the processes which take place in very small intervals of time (to tenths and even hundredths of a microsecond). This facilitated a significantly better study of the separate side of the mechanism of breakdown in liquids.

But the most progressive and fruitful thing in the past ten years has been the introduction of pulsed generators with square waves. Many experiments were conducted with them and important regularities were established. However, with such a method the experimental quantity of non-coincidences was not reduced.

Such generators can produce voltages not greater than 15-20 kv on the experimental objects. Therefore, from necessity, very small spark gaps were studied. Here the experimental technique became more complicated, and in practice less valuable results were obtained.

At the present stage of development of investigation of electrical density of liquids a highly restrictive factor is the absence of such generators for voltages of several hundred kilovolts. The opposite may also be said of the weak introduction of reliable schemes for the undistorted illustration of breakdowns by cathode oscillograms with sweeps of 10^{-8} seconds for the whole screen.

In spite of the abundance of data, the mechanism of breakdown in liquids, and also the mechanism of current increase in strong electrical fields, the reduction of E_{br} in prolonged applied voltage, etc., still remains not completely clear.

At the present time the solution of many practical important problems is solved by preliminary experiments. From them an increase of the electrical strength even of very well purified isolated liquids may be implied by introducing in them specified chemical compounds or oxygen. Such problems are applicable, for example, to transformer oil; it would follow to solve simultaneously with the problem of aging of isolation for prolonged work in conditions which would be more difficult or close to being used.

It was known long ago that the content of air in isolated liquids reduces their electrical strength. This becomes especially noticeable in the phenomenon of gas bubbles. However, the mechanism of gas formation in well-degassed isolated liquids in switching on the voltage and even at the present time remains unknown. There is no general opinion also on the mechanism of formation of gas bubbles, and also on the conditions of the phenomenon in them of impact ionization and breakdown formation.

No opinion has been reached on the exclusive importance of the method of processing liquids, i.e., chemical and mechanical purification, drying, and degassification. But meanwhile, as in passing it appears that in short pulses and small spark gaps all these methods do not exert a noticeable on E_{br}, i.e., the liquids as it were, lose their individuality.

In the conditions where they are intended for apparatus with short impulses, problems related to purification have a practical interest. However, it is not yet clear what conclusions may be made from the indicated experimental fact.

Not so long ago it was shown that in a breakdown voltage of the liquid a significant influence is offered by the material of both electrodes. This influence is related to the formation of isolated or semi-isolated films on the surface of the metal but it is not yet studied and its mechanism in many relations is not clear. Such questions should present interest for persons studying the development and preparation of electrical condensors with specified floodings or impregnated dielectrics. In connection with these one can point also to the weakly studied phenomenon of cold emission of electrons from metal in dielectric media.

In studying pre-breakdown processes it was noted that during the time of breakdown delay, in the liquids cascades are formed and low-powered streams, which do not induce a progressive breakdown in the liquid and are inhibited by opposing factors. From a practical point of view these processes can be examined as signals of the onset of breakdown. Apparently, they can be divided and used to shut off apparatus until breakdown.

There is very little data on the values of E_{br} of isolated liquids in which square pulses of various length for distances between the electrodes upon fractions of a millimeter up to several centimeters. The same may be said on the influence of the chemical composition of liquids and their structure upon E_{br}; upon the processes of spark heating; on the delay in breakdowns of large spark gaps, etc. There are very many such unsolved and practicall important problems. By considering several of them the author wanted to call attention to the large, complicated and interesting problem of the electric strength of liquid dielectrics.

LITERATURE

1. Френкель Я. И., «Электричество», 1947, 8, 5.
2. Френкель Я. И., Научно-техническая секция по электрической изоляции, Госэнергоиздат, 1949, 33.
3. Reiss K. A., Ann. Phys., 1937, 4, 325.
4. Френкель Я. И., Теория жидкого состояния, Изд. «Правда», 1943.
5. Данилов В. И., Строение и кристаллизация жидкостей, Изд. АН УССР, Киев, 1956.
6. Steward G. W., Rev. Modern Phys., 1930, 2, 116.
7. Müller A., Trans. Farad. Soc., 1933, 29, 990.
8. Warren B. E., Phys. Rev., 1933, 44, 969.
9. Blatchford A. H., Proc. Phys. Soc. (London), 1933, 45, 493.
10. Смуров А. А., Электротехника высокого напряжения и передачи электроэнергии, Гос. науч.-тех. изд., 1932, т. 1, 215.
11. Meyer H., Ann. Phys., 1930, 5, 701.
12. Bernal J. D., Fowler R. H., J. Chem. Phys., 1933, 1, 515.
13. Приходько Н. А., Труды Сибирского физико-технического института, 1942, 11, 2.
14. Kronig R., Vooren, Physica, 1942, 9, 139.
15. Kronig R., Ztschr. Phys., 1942, 118, 452.
16. Joung D. B., J. Appl. Phys., 1950, 21, 3, 222.
17. Иоффе А. Ф., Физика полупроводников, Изд. АН СССР, 1957, 178.
18. Crowe R. W., Bragg J. K., Sharbaugh A. H., J. Appl. Phys., 1954, 25, 3, 392.
19. Steward G. W., Phys. Rev., 1928, 31, 174; 1928, 32, 153.
20. Sharbaugh A. H., Bragg J. K., Crowe R. W., J. Appl. Phys., 1955, 26, 4, 434.
21. Crowe R. W., Sharbaugh A. H., Bragg J. K., J. Appl. Phys., 1954, 25, 1480.
22. Solvage B., Proc. IEE, 1951, 98, P. IV.
23. Sharbaugh A. H., Crowe R. W., Bragg J. K., J. Appl. Phys., 1953, 24, 814.
24. Lewis T. J., J. Appl. Phys., 1956, 27, 645.
25. Hippel A., J. Appl. Phys., 1937, 12, 815.
26. Joung D. B., J. Appl. Phys., 1950, 21, 3, 222.
27. Lewis T. J., Proc. IEE, 1957, P. B, 104, N 17, 493.
28. Sharbaugh A. H., Crowe R. W., Cox E. B., J. Appl. Phys., 1956, 27, 7, 806.
29. Воробьев А. А., Калганов А. Ф., Известия Томского политехнического института, 1956, 83, 248.
30. Воробьев А. А., Калганов А. Ф., ЖФХ, 1955, 29, 11.
31. Киреев В. А., Курс физической химии, Госхимиздат, 1951.
32. Оболенцев Р. Д., Физические константы углеводородов, жидких топлив и масел, Гостоптехиздат, 1953.
33. Lewis T. J., J. Appl. Phys., 1957, 28, 4, 303.
34. Mussel E., Nikuradse A., Ulbricht R., Ztschr. angew. Phys., 1956, 8, 1.
35. Edwards W. D., Canad. J. Phys., 1951, 29, 310.
36. Добрецов Л. Н., Электронная и ионная эмиссия, Гос. изд. тех.-теор. лит., 1952, 90.
37. Tropper H., J. Electrochem. Soc., 1961, 108, 2, 144.
38. Susuki M., Fujioka R., Electrotech. J., 1940, 4, 274.
39. Ruhle F., Arch. El., 1941, 35, 490.
40. Boothe D. H., Jonson O. S., Conf. Int. Grands Res. Electr., 1954, 2, 122.
41. Sletten A. M., Nature, 1959, 183, 311.
42. Swan D. W., Lewis T. J., J. Electrochem. Soc., 1960, 107, 3, 180.
43. Swan D. W., Lewis T. J., Proc. Phys. Soc. (London), 1961, 78, P. 3, N 501, 448.
44. Никурадзе А., Жидкие диэлектрики, ОНТИ, 1936, 205.
45. Лазарев А. М., ЖТФ, 1931, 4, 5, 938.
46. Рот А., Техника высоких напряжений, Госиздат, 1930, 177.
47. Вальтер А. Ф., Чолюскина, ЖТФ, 1936, 6, 11, 1910.
48. Лазарев А. М., Нигматуллина Л. И., ЖТФ, 1937, 7, 18—19, 1913.

49. Андрианов К. А., Скипетров В. В., Синтетические жидкие диэлектрики, Госэнергоиздат, 1952.
50. Ренне В. Т., Электрические конденсаторы, Госэнергоиздат, 1959.
51. Долгов Б. Н., Худобин Ю. И., Харитонов Н. П., Изв. АН СССР, отдел хим. наук, 1958, 113.
52. Долгов Б. Н. и др., Изв. АН СССР, отдел хим. наук, 1959, 7, 1238.
53. Обаданян Г. В., Пономаренко В. А., Петров А. Д., «Успехи химии», 1961, 30, 3, 1.
54. Almy J., Ann. Phys., 1900, 1, 4, 508.
55. Гиндин Л. Г., Мороз Л. М., Путилова И. Н., Френкель Я. И., ДАН СССР, 1950, 74, 1, 49.
56. Kao K. C., Higham J. B., J. Electrochem. Soc., 1961, 108, 6, 522.
57. Koppelman F., Ztschr. techn. Phys., 1935, 16, 126.
58. Clark F. M., J. Franklin Inst., 1933, 216, 429.
59. Hirano S., J. IEE, Japan, 1943, 63, 369.
60. Gemant A., Ztschr. techn. Phys., 1928, 9, 398.
61. Tropper H., Proc. IEE, 1953, 100, P. II-A, 178.
62. Sorge J., Arch. El., 1924, 13, 189.
63. Friese, Wissen. Veröffen. Siem.-Konz., 1921, 1, 41.
64. Kock F., ETZ, 1915, 36, 85 и 99.
65. Александров А. П., Вальтер А. Ф. и др., Физика диэлектриков, Гос. тех-теор. изд., 1932, 346.
66. Gazzana-Priaroggia P., Palandri G., J. Electrochem. Soc., 1960, 107, 11, 894.
67. Basseches H., Barrea M. W., Ind. Eng. Chem., 1958, 50, 6, 959.
68. Beaven G. H., Cockburn J. A., Thomson C. N., Ind. Petrol., 1949, 35, 738.
69. Hakim S. S., Higham J. B., Proc. Phys. Soc., 1962, 80, N 513, 190.
70. Moulcner G., Comtes Rendus, 1941, 213, 602.
71. Pao C. S., Phys. Rev., 1943, 64, 60.
72. Richards E. W. T., Proc. Phys. Soc (London), 1953, A66, 631.
73. Балыгин И. Е., «Инженерно-физический журнал», 1960, 3, 54.
74. Adamczewski M. J., Ann. Phys. (Paris), 1937, 8, 309.
75. Gemant A., Ztschr. Phys., 1925, 33, 789.
76. Droeger K., Arch. El., 1924, 13, 336.
77. Nikuradse A., Arch. El., 1928, 20, 403.
78. Nikuradse A., Phys. Ztschr., 1928, 31, 778.
79. Nikuradse A., Arch. El., 1929, 22, 303.
80. Nikuradse A., Arch. El., 1931, 25, 826.
81. Torijama J., Shinohara, Phys. Rev., 1937, 51, 8, 680.
82. Watson P. K., Higham J. B., Proc. IEE, 1953, 100, P. II-A, 163.
83. Hayden, Eddy, J. Amer. IEE, 1922, 138, 403.
84. Näher R., Arch. El., 1929, 21, 169.
85. Сканави Г. И., Физика диэлектриков, Гос. изд. физ.-мат. лит., 1958, 273.
86. Hancox R., Tropper H., Proc. IEE, 1957, Sept., Paper, N 2403 M.
87. Progress in Dielectrics, v. 1, London, 1959.
88. Coehn, Raydt, Ann. Phys., 1909, 4, 30, 777.
89. Балыгин И. Е., ЖЭТФ, 1956, 30, 3, 464.
90. Lewis T. J., Proc. IEE, 1953, 100, P. II-A, 141.
91. Goodwin D. W., Macfadyen K. A., Proc. Phys. Soc. (London), 1953, 66, P. 2, N 398, B. 85.
92. Spath W., Arch. El., 1923, 12, 331.
93. Torijama J., Arch. El., 1927, 19, 31.
94. Пик Ф. В., Диэлектрические явления в технике высоких напряжений, Гос. науч.-тех. изд., 1934.
95. Сиротинский Л. И., Техника высоких напряжений Госэнергоиздат, 1940, 343.
96. Schröter F., Arch. El., 1923, 12, 67.
97. Inge L., Walter A., Arch. El., 1930, 23, 279.
98. Show L., Proc. Phys. Soc. (London), 1908, 20, 220.
99. Jajasekara W. P., Ph. D. Thesis, University of London, 1957.
100. Maksiejewski J. L., Tropper H., Proc. IEE, 1954, P. II, 101, N 8, 183.
101. Балыгин И. Е., «Электричество», 1954, 1, 69.
102. Edwards, Goodlet, Perry, J. Amer. IEE, 1931, 414, 693.

103. Комельков В. С., ДАН СССР, 1945, 47, 4, 269.
104. Комельков В. С., ЖТФ, 1961, 31, 8, 948.
105. Балыгин И. Е., ЖТФ, 1953, 23, 11, 1950.
106. Tetzer V., Arch. El., 1958, 44, 1, 52.
107. Tetzer V., Arch. El., 1959, 44, 2, 6.
108. Whithead S., Dielectric Phenomena, II, London, 1928.
109. Marx, Arch. El., 1928, 20, 589; 1930, 24, 61.
110. Вальтер А. Ф., Инге Л. Д., ЖТФ, 1934, 4, 9, 1669.
111. Macfadyen K. A., Edwards W. D., Nature, 1949, 163, 171.
112. Crowe R. W., J. Appl. Phys., 1956, 27, 2, 156.
113. Hirobe T., Ogawa W., Kybo S., Electrician, 1921, 86, 2233.

114. Воробьев А. А., Приходько Н. А., Труды Сибирского физико-технического института, 1936, 4, 3, 112.

115. Смуров А. А., «Вестник экспериментальной и теоретической электротехники», 1928, 7, 8.

116. Clark F. M., Gen. El. Rev., 1951, 2, 11.

117. Волькенштейн Ф. Ф., Пробой жидких диэлектриков, Гос. изд. тех.-теор. лит., 1934, 40.

118. Koppelman, Arch. El., 1932, 26, 3.
119. Koppelman, Naturwiss., 1930, 16. 33.
120. Koppelman, ETZ, 1930, 42, 1451.
121. Koppelman, Arch. El., 1931, 25, 779.
122. Вальтер А. Ф., Инге Л. Д., ЖТФ, 1932, 2, 7.
123. Ieda Minoru, Mem. Fac. Engang Nagoja Univ., 1957, 9, 174 и 180.

124. Engelhardt V., Arch El., 1924, 13, 181.

125. Lewis T. J., Proc. Phys. Soc. (London), 1953, B. 66, N 401, 425.

126. Lewis T. J., J. Electrochem. Soc., 1960, 107, 3.

127. Zein M. E., El-Dine, Tropper H., Proc. IEE, 1956, 103, P. C. 35.

128. Hancox R., Nature, 1956, 178, 1305.
129. Solvage B., J. El. Eng. (London), Monograph., 1951, 2.
130. Проблемы современной физики, I, Электронная и ионная эмиссия, Изд. иностр. лит., 1953, 216.

131. Энгель А., Штенбек М., Физика и техника электрического разряда в газах, т. I, Объед. научно-тех. изд. НКТП СССР, 1936.

132. Dornte R. W., J. Appl. Phys., 1939, 10, 514.
133. Hancox R., Brit. J. Appl. Phys., 1957, 8, 476.
134. Williams R. L., Canad. J. Phys., 1957, 35, 134.
135. Malkin M. S., Schultz H. L., Phys. Rev., 1951, 83, 1051.
136. Sharbaugh A. H., Crowe R. W., Cox E. R., Auer P. L., Annual Report 1955 Conf. on Electr. Insulation, Washington Nation Research Council, 1956, 16.

137. Hippel A., Alger, Phys. Rev., 1949, 79, 127.
138. Балыгин И. Е., Ярушкин В. Д., ЖТФ, 1958, 28, 4, 761.
139. Балыгин И. Е., Поровский К. С., ЖТФ, 1957, 27, 3, 513.

140. Балыгин И. Е., ЖТФ, 1957, 27, 6, 1229.
141. Vick F. A., Seince Prog., 1955, XLIII, 170, 267.
142. Schumann W. O., Vertr. Ber. d. Stud. Hochspannungsanlagen, 1926.

143. Fowler R. H., Nordheim L., Proc. Roy. Soc., 1928, A, 119, 173.

144. Лукирский П. И., Изв. АН СССР, серия физ., 1944, 8, 4, 1226.

145. Benjamin M., Jenkis R. O., Proc. Roy. Soc., 1940, 176, 262.

146. Векшинский С. А., ЖТФ, 1940, 10, 1359.
147. Green W. B., J. Appl. Phys., 1955, 26, 10, 1257.
148. Vernon, Wormwell, Nurse, J. Iron and Steel Inst. (London), 1944, 150, 2. 81.

149. Tropnell B. M., Proc. Roy. Soc. (London), 1953, A218, 566.
150. Preston G. D., Bircumshow L. L., Phil. Mag., 1935, 7, 20, 706.

151. Bragg J. K., Sharbaugh A. H, Crowe R. W., J. Appl. Phys., 1954, 25, 3, 382.

152. Sato T., Nagano Sh., Torijama J., Brit. J. Appl. Phys., 1956, 7 8, 297

153. Френкель Я. И., ЖЭТФ, 1938, 12, 1292.
154. Becker, Wissen. Veröfen. Siem.-Konz., 1926—27, 6, 160.
155. Adamczewski, Nature, 1937, 137, 994.
156. Jaffe G., Ann. Phys., 1913, 42, 303.
157. Macfadyen K. A., Brit. J. Appl. Phys., 1955, 6, 1.
158. Macfadyen K. A., Hellivele G. C., J. Electrochem. Soc., 1959, 106, 12, 1022.
159. Javitz A. E., Electr. Manufacturing, 1955, 55, 6, 85.
160. Тареев Б. М., Воздействие радиоактивных излучений на электроизоляционные материалы, Госэнергоиздат, 1959.
161. Андрианов К. А., Высокомолекулярные соединения для электрической изоляции, Госэнергоиздат, 1951, 272.
162. Klein P. H., Mannal C., Commun. and Electronics, 1956, 22, 723.
163. Арьев А. М., Ашрафьян А. П., Физика диэлектриков, Труды 2-й Всесоюзной конф., Изд. АН СССР, 1961, 503.
164. Колономойцев Ф. И., Мицкевич П. К. и др., Физика диэлектриков, Труды 2-й Всесоюзной конф., Изд. АН СССР, 1960, 510.
165. Андрианов К. А., Сидорова Е. В., Совол, Госэнергоиздат, 1938.
166. Андрианов К. А., Совол и совтол, Госэнергоиздат, 1941.
167. Сканави Г. И., Физика диэлектриков, (область слабых полей). Гос. изд. тех.-теор. лит., 1949, 350.
168. Богородицкий Н. П., Муляр П. А., «Электричество», 1955, 10, 35.
169. Warner A., El. Eng., 1953, 1, 68.
170. Warner A., Trans. AIEE, 1952, 71, 330.
171. Hutchinson G. W., Nature, 1948, 162, 610.
172. Davidson N., Larsh A. E., Phys. Rev., 1948, 74, 220.
173. Davidson N., Larsh A. E., Phys. Rev., 1950, 77, 706.
174. Бах Н. А., Сборник работ по радиационной химии, Изд. АН СССР, 1955, [illegible]
175. Эмануэль Н. М., ДАН СССР, 1956, 111, 6, 1286.
176. Хмельницкий Ю. Л., Проскурнин М. А., Воренко Е. В., Труды 1-го Всесоюзного совещ. по радиационной химии, Изд. АН СССР, 1957.
177. Черножуков Н. И., Крейн С. Э., Окисляемость минеральных масел, Гос. науч.-тех. изд. нефтяной и горнотопливной лит., 1955, 46.
178. Booser E., Fenske M., Ind. Eng. Chem., 1952, 44, 8, 1850.
179. Heyden, Typke, Petrol., 1926, 23, 1024.
180. Frank, Немецкий патент, 1919, № 365378.
181. Anderson, ASEA J. (Allmänna Svenska elektr. aktiebologet Jour.), 1924, 11, 12, 123.
182. Stäger, Isoliermaterialen, 1931, 46.
183. Cragoce, Hadnett, Trans. AIEE, 1925, 44, 219.
184. Черножуков Н. И., Крейн С. Э., Лосиков Б. В., Химия минеральных масел, Гостехиздат, 1959.
185. Mauren et Dufroisse, Chem. Rev., 1926, 3, 113.
186. Семенов Н. Н., Цепные реакции, Госхимтехиздат, 1939.
187. Mead, Ind. Eng. Chem., 1927, 17, 11.
188. Tanaka, Nakumura, J. Soc. Chem. Ind. Japan, 1930, 107B, 8; 1930, 4, 126B; 1931, 10, 405B.
189. Denison, Condi, Ind. Eng. Chem., 1945, 37, 1102.
190. Haslem, Frolich, Ind. Eng. Chem., 1927, 17, 2.
191. Wasson, Smith, Ind. Eng. Chem., 1953, 45, 197.
192. Крейн С. Э., Стабилизация турбинных и трансформаторных масел, Госэнергоиздат, 1948.
193. Иванов К. И., Вилянская Е. Д., «Химия и технология топлив и масел», 1957, 4.
194. Assafa, Balsbaugh, Ind. Eng. Chem., 1943, 35, 8, 909.
195. Peterson, Trans. ASME (Amer. Soc. Mechan. Eng.), 1943, 64, 3, 227.
196. Иванов В. С., Повышение качества и применение смазочных материалов (сборник докладов), Гостоптехиздат, 1957, 120.
197. Качалинский В. А., Современные методы производства смазочных масел, Госхимтехиздат, 1947.
198. Воробьев А. А., Техника высоких напряжений, Госэнергоиздат, 1945.
199. Eisler H., Ztschr. techn. Phys., 1937, 18, 2, 23.
200. Волощенко Н. Ф., «Электричество», 1947, 8.

201. Комельков В. С., Лифшиц А. М., Изв. АН СССР, отдел. тех. наук, 1950, 10, 1463.
202. Мантров М. И., «Электричество», 1940, 9, 56.
203. Балыгин И. Е., «Электричество», 1956, 7, 63.
204. Marx E., Lichtbogen-Stromrichter, Berlin, 1932, 9.
205. Сиротинский Л. И., Техника высоких напряжений, Госэнергоиздат, 1951, I, 127.
206. Quincke G., Wied. Ann., 1895, 54, 385.
207. Schröder J., Ann. Phys., 1909, 29, 125.
208. Nikuradse A., Ztschr. Phys., 1932, 77, 216.
209. Nikuradse A., Naturwiss., 1931, 19, 233.
210. Беркс Д. Б., Шулман Д. Г., Прогресс в области диэлектриков, Госэнергоиздат, 1962, т. 1, 137.
211. Ruhle F., Phys. Ztschr., 1943, 44, 89.
212. Baker E. H., Boltz H. A., Phys. Rev., 1937, 51, 275.
213. Le Page, Du Bridge, Phys., Rev. 1940, 58, 61.
214. Dornte R. W., Ind. Eng. Chem., 1940, 32, 1529.
215. House H., Proc. Phys. Soc. (London), 1957, 70, 913.
216. Morant M. J., Proc. Phys. Soc. (London), 1955, 68, 51, 513.
217. Plumley H. J., Phys. Rev., 1937, 52, 140.
218. Plumley H. J., Phys. Rev., 1941, 59, 200.
219. Nikuradse A., Russischwilli, Ann. Phys., 1931, 8, 811.
220. Schuman W. O., Arch. El., 1923, 12, 801.
221. Watson P. K., Sharbaugh A. H., J. Electrochem. Soc., 1960, 107, 6, 516.
222. Остроумов Г. А., ЖЭТФ, 1956, 30, 2, 282.
223. Остроумов Г. А., ЖТФ, 1954, 24, 10, 1915.
224. Остроумов Г. А., ЖЭТФ, 1961, 41, 2, 441.
225. Иоффе А. В., Иоффе А. Ф., ЖЭТФ, 1939, 9, 1428.
226. Poole H., Phil. Mag., 1916, 32, 112.
227. Пружинина-Грановская В. И., ЖЭТФ, 1937, 7, 508.
228. Пружинина-Грановская В. И., ЖЭТФ, 1940, 8, 125.
229. Schiller H., Arch. El., 1927, 17, 609.
230. Горелик Б. В., Дмитриев В. Т., ЖТФ, 1948, 3, 333.
231. Onsager, J. Chem. Phys., 1934, 2, 599.
232. Fröhlich H., Proc. Roy. Soc., 1947, 188, 521, 1015.
233. Saxe R. F., Lewis T. J., Brit. J. Appl. Phys., 1955, 6, 6, 211.
234. Ward B. W., Lewis T. J., J. Electrochem. Soc., 1960, 107, 3, 191.
235. Allibone T. E., Meek J. M., Proc. Roy. Soc., 1938, 169, 937.
236. Капцов Н. А., Электрические явления в газах и в вакууме, Гос. изд. техн. лит. 1950, 582.
237. Jamanaka C., Suita T., J. Phys. Soc. Japan, 1953, 8, 277.
238. Darveniza M., Nature, 1959, 183, 743.
239. Балыгин И. Е., ЖТФ, 1960, 30, 4, 441.
240. Балыгин И. Е., ЖТФ, 1958, 28, 4, 767.
241. Балыгин И. Е., Изв. АН СССР, серия физ., 1958, 22, 4, 427.
242. Балыгин И. Е., ЖЭТФ, 1953, 25, 6 (12) 738.
243. Балыгин И. Е., ДАН СССР, 1954, XCV, 4, 745.
244. Уотерс У., Химия свободных радикалов, Изд. иностр. лит., 1948, 17.
245. Марек Л. Ф., Ган Д. А., Каталитическое окисление органических соединений, ОНТИ, 1936, 39.
246. Liao T. W., Anderson J. G., Amer. IEE, P. I, 1953, 72, 641.
247. Балыгин И. Е., «Электричество», 1949, 7.
248. Брагин С. М., Вальтер А. Ф., Семенов Н. Н., Пробой диэлектриков, Госиздат, 1929, 257.
249. Hippel A., Trans. Farad. Soc., 1946, 42A, 78.
250. Fröhlich H., Proc. Roy. Soc., 1937, 160, 230.
251. Жданов В. А., Труды Сибирского физико-технического института, 1942, 2, 135.
252. Балыгин И. Е., ЖТФ, 1954, 24, 3, 737.
253. Балыгин И. Е., ЖЭТФ, 1953, 24, 5, 562.
254. Сиротинский Л. И., Техника высоких напряжений, ч. I., Госэнергоиздат, 1953.
255. Кобеко П. П., Аморфные вещества, Изд. АН СССР 1952, 17.
256. Лифшиц И. М., Пекар С. И., УФН, 1955, 6, 4, 531.
257. Тамм И. Е., Sow. Phys., 1932, 1, 733.
258. Балыгин И. Е., Известия высших учебных заведений, «Физика», 1958, 5, 41.
259. Балыгин И. Е., ЖТФ, 1957, 27, 10, 2291.

260. Балыгин И. Е., Физика диэлектриков, Труды 2-й Всесоюзной конф., Изд. АН СССР, 1960, 262.
261. Rorden H., Amer. IEE, 1932, Sept., 825.
262. Балыгин И. Е., ЖЭТФ, 1954, 26, 1, 98.
263. Bloisse B. S., Boogoart A., Van den Erze F., Bull. Inst. intern. froind, 1958, 1, 333.
264. Балыгин И. Е., Физика диэлектриков, Тр. 2-й Всесоюзной конф., Изд. АН СССР, 1960, 271.
265. Anderson, Astroph. J., 1920, 1, 37.
266. Мандельштам С. Л., Суходрев Н. К., ЖЭТФ, 1953, 24, 701.
267. Долгов Г. Г., Мандельштам С. Л., ЖЭТФ, 1953, 24, 691.
268. Арцимович Л. А., Андриянов А. М. и др., «Атомная Энергия», 1956, 3, 76.
269. Залесский А. М., Электрическая дуга отключения, Госэнергоиздат, 1963, 41.
270. Балыгин И. Е., «Инженерно-физический журнал», 1960, 3, 6, 19.
371. Леб Л., Основные процессы электрических разрядов в газах, Гос. изд. тех-теор. лит., 1950, 516.
272. Абрамсон И. С., Маршак И. С., ЖТФ, 1942, 12, 632.
273. Бурьянов Б. П., Трансформаторное масло, Госэнергоиздат, 1955, 66.
274. Глинка Н. А., Общая химия, Госхимиздат, 1954, 228.
275. Спитцер Л., Физика полностью ионизированного газа, Изд. иностр. лит., 1957, 45.
276. Langevin P., Ann. d. Chem. et Phys., 1903, 28, 317,
277. Гегечкори Н. М., ЖЭТФ, 1951, 21, 4, 501.
378. Драбкина С. И., ЖЭТФ, 1951, 21, 4, 473.
279. Früngel F., Optik Ztschr. Gebit der Licht und Elektronenoptik, Stuttgart, 1948, 3, 1/2, 124.
280. Абрамсон И. С., Гегечкори Н. М. и др., ЖЭТФ, 1947, 17, 862.
281. Sehal R., Ztschr. angew. Phys., 1950, 2, 6, 252.
282. Покровский Г. И., Станюкович К. П., Изв. АН СССР, серия физ., 1944, 8, 4, 214.
283. Балыгин И. Е., «Электричество», 1949, 4, 73.
284. Юткин Л. А., Электрогидравлический эффект, Машгиз, 1955.
285. Рой Н. Н., Фролов Д. П., ДАН СССР, 1958, 118, 4, 683.
286. Комельков В. С., Скворцов Ю. В., ДАН СССР, 1959, 129, 6, 1273.
287. Скворцов Ю. В., Комельков В. С., Кузнецов Н. М., ЖТФ, 1960, 30, 10, 1165.
288. Ландау Л. Д., Лифшиц Е. М., Механика сплошных сред, Гос. изд. тех.-теор. лит., 1954, 17.
289. Зингерман А. С., ЖТФ, 1956, 26, 11, 2531.
290. Бриджмен П., Физика высоких давлений, Науч.-тех. изд. НКТП СССР, 1935, 134.
391. Корнфельд М., Упругость и прочность жидкостей, Гос. изд. тех.-теор. лит., 1951, [illegible].
292. Maxwell J. C., Phil. Trans. Roy. Soc., A, 1866, 8[illegible], 157.
293. Корнфельд М., Рывкин М. М., ЖЭТФ, 1939, 9, [illegible]
294. Fröhlich H., Phys. Rev., 1939, 56, 349.
295. Callen H. B., Phys. Rev., 1949, 76, 1325.
296. Seitz F., Phys. Rev., 1949, 76, 1376.
297. Emanueli, El. World, 1927, 90, 691,
298. Horowitz, Arch. El., 1927, 18, 583.
299. Gemant A., Ztschr. techn. Phys., 1929, 9, 393.
300. Gemant A., Wiss. Veröffen. Siem.-Konz., 1927, 6, 87.
301. Edler, Arch. El., 1930, 24, 37.
302. Семенов Н. Н., Вальтер А. Ф., «Журнал прикладной физики», 1929, 6, 6.
303. Sharbaugh A. H., Devins J. C., El. Technol., 1961, 68, 4, 107.
304. Güntherschulze, Jahrbuch der Radioactiv. und Elektronik, 1922, 19, 92.
305. Güntherschulze, Über die dielektr. Festigkeit, München, 1924.
306. Böning P., Ztschr. Fernmeldt, 1928, 9, 161.
307. Böning P., Ztschr. techn. Phys., 1939, 20, 43.
308. Флоренский П. А., «Вестник электротехники», 1929, 5—6, 63.

309. Волькенштейн Ф. Ф., ЖТФ, 1934, 4, 6, 954.
310. Przibram K., Phys Ztschr., 1904, 5, 574.
311. Swan D. W., Proc. Phys. Soc., 1961, 78, P. 3, N 501, 423.
312. Gzowski O., Terlecki J., Acta Phys., Polon, 1959, 18, 191.
313. Chong P., Inuishi I., Technology Reports of the Osaka University, 1960, 10, 545.
314. Ward A. L., Phys. Rev., 1958, 112, 1852.
315. Kok J. A., Corbey M. M. G., Appl. Scient. Res., 1956, S-B, 6, 197.
316. Kok J. A., Electrical Breakdown of Insulating Liquids, Interscience Publ. INC, New Jork.
317. Kok J. A., Corbey M.. M. G., Appl. Scient. Res., 1957, S-B, 6, 449.
318. Lewis T. J., Brit. J. Appl. Phys., 1958, 9, 1, 30.
319. Herzbery G., Molecular Spectra and Molecular Structure, II, New York, 1945, 192.
320. Adamczewski, Zeszyty naukowe Politechniki gdańskiej, 1957, 3, 3.
321. Atwood S. S., Bixby W. H., J. Franklin Inst., 1943, 3, 252.
322. Seeger R., Teller E., Phys. Rev., 1938, 54, 10, 515.
323. Seeger R., Teller E., Phys. Rev., 1940, 58, 8, 279.
324. Bohr N., Phil. Mag., 1913, 24, 10.
325. Френкель Я. И., Кинетическая теория жидкостей, Изд-АН СССР, 1945, 164.
326. Lewis T. J., Ward B. W., Proc. Roy. Soc., 1962, SA, 268, № 1337, 233.