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Structure Formation in Disperse Systems in an Electric Field

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The application of an electric field to disperse systems usually results in the aggregation of the particles of the dispersed phase and their organisation into characteristic structures oriented along the lines of force. Processes of this kind are observed both in finely dispersed colloidal systems and in coarsely dispersed systems–emulsions, suspensions, powders. Despite the extremely varied phenomenological picture of the structure-formation processes, which in many respects is due to the nature of disperse systems, the mechanisms and dynamics of their development also have much in common. Analysis of the fundamental mechanism and the kinetics of these processes constitute the theoretical aspect of the problem of structure formation in disperse systems in an electric field.

Apart from the purely theoretical interest, the problem does not lack practical importance. It is sufficient to say that structure-formation processes underlie phenomena such as, for example, the breakdown of liquid dielectrics and the dehydration of petroleum in an electric field.

In this review an attempt is made to give a brief outline of the historical development of the problem, to characterise its present state, and to suggest the possible ways in which it may develop further. As far as we are aware, the structure-forming effect of an electric field on disperse systems was first described by Rafinesque[1] and Hohlfeld[2], who observed the formation on the surface of a charged object of thread-like structures made up of smoke particles.

The investigations of Munk af Rosenschöld[3,4], who must be regarded as the original discoverer of the coherer and who anticipated Branly by half a century, were carried out in the 1830's. In his experiments a tube filled with wood charcoal powder in an electric circuit completed the circuit under the influence of electric discharges occurring in its vicinity; when the tube was shaken, the circuit was reopened. In the 1880's studies on the electrical conductivity of metallic powders were renewed and led to the discovery of coherers or fritter-detectors of electromagnetic

waves. The work of Calzecchi-Onesti[5] and Branly[6,7] must be mentioned as foremost among the investigations in this field. Branly's coherer consisted of a glass tube filled with metal filings and incorporated into the circuit. Since at that time coherers were the only detectors of electromagnetic waves available, they were thoroughly investigated. Towards the middle of the 1890's it became evident that, firstly, the coherer effect arises only when the conducting material is dispersed in a dielectric (gaseous, liquid, or solid), secondly, the concentration of the conducting material must be fairly high, and, finally, the effect is not entirely reversible: the greatest conductivity jump is observed when the field is first applied.

In the literature of that period three views were put forward concerning the nature of coherers. Lodge[8-10] believed that the reason for the increase of the conductivity of the powder under the action of the field is the formation of a current-conducting path (bridge) due to the aggregation of particles under the influence of electrostatic forces; these forces "strip" insulating films from the surface of the particles, in particular oxide films. According to Auerbach[11], the role of the field is purely mechanical. The field induces a relative disposition of the particles such that it ensures a higher conductivity of the powder. By virtue of surface forces, the resulting structures are maintained also after the removal of the field. Branly[12-17] believed that the layers of insulating dispersion medium between the powder particles are "modified" on application of the field and become conducting.

The adhesion of the particles under the action of electrical pulses was confirmed by numerous investigators. Thus in his study, under the microscope, of the effect of electric discharges on copper, iron, brass, and silver powders, Arons[18] observed the formation of bridges from the powder particles. Particularly stable bridges were produced in copper powders. Sundorph[19] investigated iron and nickel powders. After the powders began to conduct current readily under the action of the field, he succeeded in isolating with the aid of a weak magnet a thin bridge connecting the electrodes. In Tommasina's experiments[20,21] bridges made up of metallic particles reached lengths of 20 cm in distilled water. Using horizontal electrodes, he observed the formation of a multiplicity of vertical chains of particles which immediately collapsed as soon as one of the chains reached the opposite electrode and closed the circuit. Thus the formation of conducting bridges in the powders was demonstrated experimentally.

The problem of coherers gave rise to a number of related problems. These include in the first place the problem of the breakdown in an electric field of aerosols and emulsions. Clark and Lodge[22] noted the common features of structure-formation processes in powders and aerosols in an electric field. The industrial methods for the removal of dust from air and dehydration of petroleum (Cottrell's method and others) originate from this phenomenon also.

Studies of the conductivity of natural air gaps are also closely associated with the problem of coherers. Harden[23] observed that, when a spark jumps in a discharge unit, certain particles are brought into motion in the 6 μm electrode gap and the process terminates in the formation of a bridge. This phenomenon was investigated in greater detail by Sundorph[24]. Using apparatus with movable electrodes, he observed the formation of bridges up to 50 μm in length in a constant field. Similar phenomena were later studied by Hoffman[25], Szèkely[26], Pearson[27], and Pectow[28]. All these studies confirm the characteristic structure formation under the action of an electric field in systems whose disperse phase is a product of the breakdown of the electrode.

At the beginning of the twentieth century coherers lost their practical value with the appearance of the Braun detector; they became of less interest, and studies in this field almost ceased. The literature on coherers has been reviewed by Aschkinass[29], Branly[17], and Righi and Dessau[30].

Starting with the 1920's finely dispersed systems began to attract attention to some extent as a consequence of the interest in problems of colloidal chemistry which arose at the time. The first investigations of the threadlike structure formed in the preparation of aerosol by the electric arc dispersion method were performed during this period[31-33]. Kuczynski[34], Muth[35], and Krasny-Ergen[36] investigated structure formation in emulsions in a high-frequency field. Kuczynski and Muth described the "construction" of chains from emulsion drops along the lines of force of the field. Krasny-Ergen calculated the minimum field strength necessary to overcome the thermal motion interfering with the organisation of drops into structures; his calculations agreed with Muth's experimental data. Pauli and coworkers[37,38] observed an increase of the conductivity of a gold hydrosol after prolonged passage of a current, due to the formation of chain structures.

Kruyt and Vogel[39] made a detailed study of structure formation in hydrosols in an alternating field. They studied gold, platinum, silver, copper, silver iodide, vanadium pentoxide, and paraffin hydrosols and also an aqueous emulsion of tetralin. According to their data, structure formation begins with the precipitation of particle aggregates on the electrode, after which branching structures, chains made up of particles similar to those observed in Pauli's experiments, grow from these deposits towards one another. When the chains are joined, the conductivity of the system increases by a factor of several tens. The higher the field strength the more rapid is the growth of the chains and the larger the gap between the electrodes which they can bridge. Under the microscope it is seen that the structured sol consists of a liquid traversed by a multiplicity of very thin intertwined and knotted threads forming a net-like structure. After the removal of the field the structure breaks down into individual fragments, consisting of many particles. The formation of chains is interfered with by bubbles produced, according to Kruyt and Vogel[39], as a result of the evaporation of water under the action of Joule heat. It was established, that on going from noble metals to copper, the capacity for the formation of threads falls. They rarely appear in copper sols and do not appear at all in silver iodide and vanadium pentoxide sols. In water–paraffin and water–tetralin systems the formation of bead-like aggregates from the dispersed dielectrics is again observed. Later the formation of similar structures was observed by Stauff[40], Us'yarov and coworkers[41-42] (in an alternating field), and also Pearce and Mech (in a constant field)[43]. Kruyt and Vogel distinguished bead-like structures (Perlschnurbildungen) formed from dielectrics and chains (Ketten) formed from metallic particles in accordance with the type of bond linking the units together: the bead-like structures broke down completely after the removal of the field, while the chains broke down into fragments consisting of many particles. According to Kruyt and Vogel, polarisation forces play a major part in the formation of chains; after the deformation and breakdown of the ionic shells of the micelles, van der Waals's cohesion forces begin to act. Subsequently recrystallisation processes develop at the site of direct contact between the nuclei, which accounts for the relative stability of the chains after the removal of the field.

We shall now consider the studies on aerosols performed during that period. These include primarily the work of

Beischer[44] on the stability of structures formed in aerosols of Fe_2O_3, ZnO, As_2S_3, NH_4Cl, iron, anthracene, and aminoazobenzene under the action of the field. The stability of these structures was determined from the maximum length of the chain formed in a field of about 300 V cm^{-1}, remaining attached to the electrode, without breakdown, after the removal of the field. The results were semiquantitative, since the true cross-sectional area of the chains was unknown. According to Beischer, the principal factor determining the stability is the adhesion of the particle aggregates. However, in some cases forces of a different type make a contribution: magnetic and electrostatic attraction forces (ferromagnetic aerosol of iron and the pyroelectric aerosol of aminoazobenzene) or crystal lattice bonding forces (ammonium chloride aerosol, which has a high vapour pressure at room temperature). Beischer regarded chains as tertiary formations. The primary formations are crystal nuclei and the secondary formations their spherical aggregates, which give rise to chains.

In his study of oil mists in an electric field, Winkel[45,46] failed to observe chain structures, a finding which in his view can be used to determine the state of aggregation of the disperse phase of aerosols.

Using the ultramicroscope, Artemov[47,48] studied the coagulation of the ammonium chloride aerosol in air of different humidities using a constant field. In the absence of moisture oriented branched aggregates are formed on the electrode. As the humidity increases, the aggregates grow in size and at 70% humidity drops of solution are deposited on the surface of the electrode instead of the aggregates. Artemov obtained similar results for anthraquinone and aminoazobenzene with water replaced by an appropriate solvent.

The coalescence of small droplets into larger ones is typical of mists in an electric field[49-51]. When the field is sufficiently strong, the drops are stretched into threads, which, on further increase of field strength, again break up into individual drops[52]. In many cases oriented coagulation of aerosols in an electric field takes place as a result of adsorption by the aerosols of the ions formed in air under the action of the field. Fuks[49] developed a theory of the aggregation processes in charged aerosols. Harvey et al.[53] described the formation of chain and three-dimensional network structures under the action of the field in silver and gold aerosols.

The studies on the breakdown of liquid dielectrics occupy a special place. It is known that the dielectric strength of transformer oil is lower the longer it is maintained under a potential. This phenomenon has been attributed for a long time to the aggregating effect of the field on the colloidal particles present and gradually accumulating in the oil. It has been shown in a number of studies that cellulose fibres are the most harmful in this respect, particularly in the presence of traces of water. While dry fibres lower the breakdown strength by 20%, moist fibres lower it by a factor of more than ten[54]. The explanation is that fibres which have adsorbed water are oriented along the lines of force of the field and form a bridge which is responsible for the breakdown. In the absence of fibres water has relatively little effect on the dielectric strength of the oil even when present at high concentrations.

Piper and coworkers[55] showed that, when an electric field is applied to the model phenol–liquid paraffin system, the electrical conductivity increases sharply as soon as a bridge structure consisting of acicular phenol crystals is produced.

At the beginning of the 1950's Frenkel', Gindin, Putilova, Moroz, and Shpanskaya published a series of papers on structure formation in disperse systems in a constant electric field. These studies originated from the problem of the corrosion of metals by liquid dielectrics. In the study of the mechanism of the corrosion processes in dielectrics it was found that the processes are electrochemical. It was established that electrochemical cells operate in hydrocarbon solutions of iodine or aliphatic acids and the current generated by them exceeds by several powers of ten the current which would be expected on the basis of the electrical conductivity of the initial solutions. To account for this phenomenon, it was suggested that salt bridges are formed between the electrodes during the operation of the cells, lowering thereby the internal resistance[56-58]. At the same time one of the present authors studied the suspensions of aluminium in kerosene as a possible reactive fuel and he decided to attempt to observe similar bridges in aluminium suspensions.

The first papers of the above cycle are in fact devoted to these suspensions. When a constant electric field is applied to a suspension of aluminium in petrol, the particles of the suspension begin to move, the rate of motion increasing with field strength E. Marked asymmetry of the motion is observed. Most of the aluminium particles are directed towards the cathode and cover the latter by a fairly thick layer of loose aggregates which grow in the direction of the anode. In the early stages of the process the latter remains clear. However, after a time it becomes coated by particles which have migrated from the cathode and which give rise to new aggregates growing to meet those formed earlier. Frequently the aggregates bound to the cathode suddenly break away from the latter and disintegrate into individual particles, giving the impression of small "explosions". At a certain stage of the process almost the entire space between the electrodes is filled by aggregates oriented along the lines of force of the field. Nevertheless the system is still a dielectric. However, when the field strength is increased to about 4000 V cm^{-1} (E_{cr}), electrical breakdown occurs and the system becomes conducting. This breakdown is readily observed from the sharp increase (by a factor of about 10^5) of the current in the circuit, the decrease of the field strength (from 4000 to 1 V cm^{-1}), and other effects. After the particles have fallen off, a single bridge in the form of a thin thread joining the electrodes is observed between them[59-61]. Subsequently the most important stages of the process were filmed[62,63]. Frame I in Fig. 1 shows the instant preceding the electrical breakdown. Frames II, III, and IV are pictures immediately after the breakdown associated with the formation of the bridge. The effects of the material and shape of the electrodes, the shape and size of the aluminium particles, and also the nature of the dispersion medium on the electrical breakdown were investigated[59-61]. If the bridges are not disconnected from the current source, they can exist for a long time. However, they persist even after the current has been switched off. The formation of the bridge and analysis of its behaviour suggest the presence of two types of bonds between its units. The first type is electrostatic and is observed in the stages of bridge formation preceding the electrical breakdown. The second type is a metallic bond produced at the instant of breakdown; by virtue of this bond the bridge continues to exist after the current ceases to flow. The voltage–current characteristics of the bridges[62,64] are in most cases monotonic up to the highest currents which the bridges can withstand. The initial sections of the characteristics are linear (Ohm's law holds) and then their angle of inclination to the E axis begins to decrease (the resistance increases) (Fig. 2, curve *1*). Such character-

istics are typical for metallic conductors whose temperature rises due to Joule heat.

The branches of the voltage–current characteristics obtained with rising (ascending branch) and falling (descending branch) voltage coincide in most cases (Fig. 2, curve *1*). However, sometimes this is not so (Fig. 2, curve *2*) and a characteristic hysteresis loop forms; this happens only when characteristic "flashes" occur on the current and voltage oscillograms, indicating a rearrangement of the structure of the bridges in the electric field. These and other observations confirm the hypothesis[60]

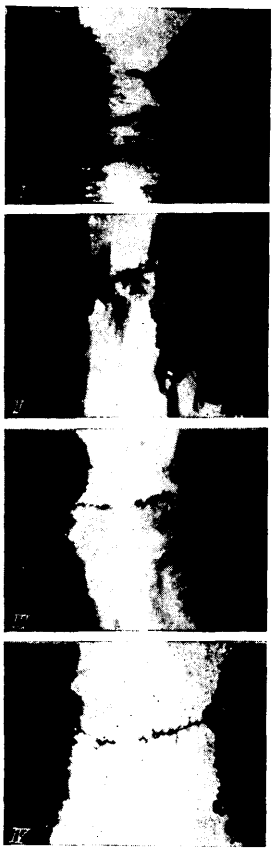


Figure 1. Film frames showing various stages in structure formation.

that the higher stability of the bridge conducting current compared with the bridge in the absence of current is due to the fact that, when the metal contact between the bridge unit breaks down, a fairly strong electric field arises and restores this contact. The bonds between the particles and the cathode, the formation of which is intrinsically responsible for the initiation of bridge formation, and the bonds between the particles themselves before electrical breakdown result from the electric polarisation of the particles. It must be emphasised that the aluminium particles are covered by thin layers of non-conducting oxide, which prevents the direct electrical contact of the particles with one another and with the electrode. Because of this, the suspension continues to be a dielectric even when the entire space between the electrodes is filled by the structures. The conversion of the system from a dielectric into a conductor occurs only when the electric field strength E reaches a value E_{cr} at which the insulating films in one of the numerous aluminium chains filling the space between the electrodes breakdown and the bridge becomes a metallic conductor. Hence follows the physical significance of E_{cr} as a measure of the breakdown voltage of the non-conducting oxide film, calculated over all the units of the bridge.

Indirect confirmation of the validity of this interpretation of E_{cr} is provided by the fact that suspensions of noble metals, for example platinum, become conductors at extremely low values of E.[65–68] Because of the very rapid precipitation of platinum particles, bridges of this metal, like those of aluminium, can be obtained only by "pulling" from the powder: a field of definite strength was established between the electrodes, after which the latter were allowed to touch the surface of a platinum powder; when the electrodes were raised, a bridge was drawn out. In contrast to the observations on the aluminium powder, the

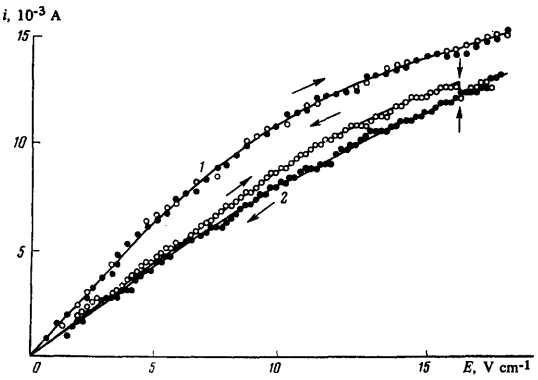


Figure 2. Voltage–current characteristics of the bridges.

platinum powder conducted current even at a minimal value of E. Evidently, it is sufficient for the platinum particles to be merely in contact with one another for the powder to behave as a conductor, since there are no bulk-phase oxide films on the surface of these particles.

Suspensions of copper, whose oxides are semiconductors, occupy an intermediate position between those of aluminium and platinum. Copper suspensions show an appreciable conductivity even at values of E much less than E_{cr} necessary for breakdown. As soon as the space between the electrodes becomes filled by structures made up of copper particles, a current appears in the circuit. A typical voltage–current characteristic for the system in this state is presented in Fig. 3, from which it follows that the conductivity of the system increases smoothly with field strength. Approximate calculations show that, when the overall field strength is only 100 V cm^{-1}, a field strength of the order of 10^4 V cm^{-1} is attained at the oxide film. Ioffe and Ioffe[69] showed that, for this value of E, the conductivity of Cu_2O increases exponentially with $\sqrt{E}$. In Fig. 3 the same relation is presented as a plot of ln σ against $\sqrt{E}$. Evidently the points lie on a straight line and therefore the relation holds in our case too. This

observation shows that before electrical breakdown we are dealing with conductivity due to the contacts between the individual copper particles when the conductivity of the system as a whole is determined by that of the surface semiconductor Cu_2O films on the particles. This is to some extent confirmed by the relation established between E_{cr} and the duration of oxidation of the copper powders

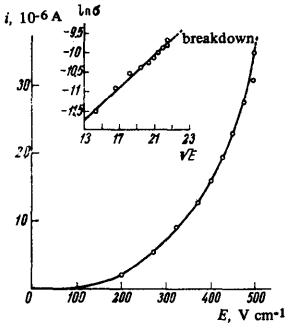


Figure 3. Electrical conductivity of suspensions and powders of oxidised copper before electrical breakdown.

(Fig. 4). The parabolic relation between these quantities is probably a consequence of the parabolic law governing the growth of oxide films. On the basis of this relation, one can set up rapid methods for the determination of the degree of oxidation of metallic powders (taking into account, of course, the characteristic features of the oxidation of each metal) [70].

Apart from the suspensions and powders of aluminium, platinum, and copper, dispersions of other metals have been investigated, namely of iron, cobalt, nickel, chromium, molybdenum, tungsten, antimony, bismuth, tin, lead,

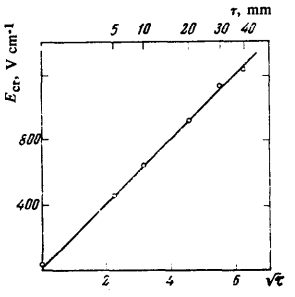


Figure 4. Variation of E_{cr} with the duration of oxidation of copper powders.

zinc, and silver. According to the behaviour of their disperse systems in an electric field, the metals can be divided into the following four groups:

1. Lead and bismuth. The suspensions of powders of these metals show some features resembling the dispersions of aluminium—almost complete absence of the conductivity of the structures before electrical breakdown.

2. Iron, cobalt, nickel, chromium, molybdenum, and tungsten. In their behaviour in an electric field, these metals resemble copper—weak conductivity before breakdown, increasing with E.

3. Tin and zinc. When an electric field is applied to suspensions of these metals, dendrite-like structures are produced, whose conductivity increases with the field even more than for the metals of the preceding group. However, the formation of a stable bridge and the electrical breakdown of the suspensions associated with it cannot be observed. Instead there is sparking with a crackling noise, accompanied by the evolution of gas bubbles—evidently products of the electrical cracking of the dispersion medium (petrol). The conductivity of the powders of these metals, due to the three-dimensional structure when $E \geqslant E_{cr}$, is replaced, like that of the metal powders of the preceding group, by the conductivity of the bridge; however, the electrical breakdown of zinc and tin powders, associated with the formation of a bridge, is not characterised so much by a jump in conductivity as by its stabilisation, i.e. the powders resemble cuprous oxide in this respect (see below).

4. Silver and antimony. Dispersions of these metals behave in an electric field in many ways similarly to the dispersions of platinum. The distinguishing features of these metals, like those of platinum, are a very low value of E_{cr} and the fact that no stable dendrite-like structures are formed in them. Although the problem requires further study (mainly quantitative), it is now clear that in general the behaviour in an electric field of the suspensions and powders of the metals investigated is determined by the nature, and in the first place by the conductivity, of their oxide films [71].

Suspensions of semiconductors such as boron carbide and cuprous oxide have also been investigated [65-68]. When a constant field is applied, the suspended particles of the carbide are deposited on the electrodes, preferentially on the anode. With increase in E, bridges begin to form in the space between the electrodes. As E rises, the number of such bridges increases, this being accompanied by a smooth rise of the current. When the apparatus is gently tapped, the bridges begin to fall off without disintegrating into smaller particles. On attainment of E_{cr}, the current increases sharply (by 2–3 powers of ten). After faulty, incomplete bridges have fallen out of the interelectrode space, a single bridge remains, which is responsible for the jump in the conductivity of the system; the form of this bridge is fairly characteristic: it is thin in the middle but thickens towards the ends attached to the electrode.

In cuprous oxide suspensions the formation of a bridge is also accompanied by a sharp rise of the conductivity of the system, but the attainment of E_{cr} is shown in cuprous oxide suspensions not so much by an increase of current (the latter increases only by a factor of two) as by its stabilisation.

Suspensions of soaps (the stearates of barium, zinc, nickel, cobalt, and copper and barium oleate) in aviation fuel and in liquid paraffin and also suspensions of a protein (egg albumin) in petrol have been investigated [65-68,72] in addition to the suspensions of metals and semiconductors. Outwardly the structure-formation processes in these systems are to some extent similar to those observed in suspensions of metals and semiconductors. When the cuvette with a suspension of soap and protein is included in a high-voltage circuit, the suspended particles begin to move rapidly. Then the particles of soaps (at $E = 7500$ V cm^{-1}) and hydrated protein form characteristic ribbon-like struc-

tures, the number of ribbons increasing with field strength. The formation of ribbons from protein begins at both electrodes but soap ribbons are produced predominantly from one electrode only; when the ribbons break away accidentally, their portions tend to migrate to the opposite electrode, where they become attached and initiate the growth of new ribbons. Sometimes the ribbons also grow in width, their edges coming into contact. The length of the ribbons reaches 1 mm and more, their width is 4–40 μm, and their thickness is of the order of 1 μm. The instant when the electrodes are joined together by the ribbons is shown by a sharp (approximately by 1–2 powers of ten) increase of the conductivity and a corresponding decrease of field strength. The study in polarised light of freshly prepared zinc stearate ribbons showed that they have an anisotropic structure, which, however, disappears after a time. When a field is applied to a suspension of dry albumin in petrol, the protein particles are drawn into the space between the electrodes and, becoming arranged along the lines of force of the field, form structures in which they do not adhere to one another but are merely in contact. It may be suggested that the conductivity of the ribbon-like structures from the soaps and the protein (under the usual dielectric conditions) is ionic and is of the surface and not bulk-phase type: in a later study[73] conductivity of this type was observed for lithium stearate suspensions in a mineral oil; it was explained by the presence of traces of moisture on the surface of the soap fibres.

Skanavi[74] noted that: "the suspension of a metal in a liquid dielectric constitutes to some extent a simplified model of a contaminated liquid. Therefore studies of this kind are not only of specialised interest, but they permit an approach to a more detailed examination of the problem of the mechanism of electrical breakdown and in particular the formation of conducting bridges or channels in contaminated liquid dielectrics... Before the electrical breakdown of a contaminated liquid containing conducting particles, a low-resistance bridge, joining the electrodes, is formed".

Similar views were later expressed by Kok and coworkers[75-80]. Incidentally, they suggested that, in order to enhance the dielectric strength of insulating oils, surface-active additives preventing the formation of bridges be used. They derived a relation between the "threshold" field strength at which the stable bridges are formed and the size of the colloidal particles of the admixture in the dielectric. The results of experiments on the electrical breakdown of liquid argon, nitrogen, and oxygen, proved to be close to the calculations.

Using the idea of the formation of conducting bridges from individual particles under the action of an electric field, Florek and Skowronski[81] constructed a discharge unit for the purification of liquid dielectrics.

Deinega and Vinogradov[82-85] investigated the effect of the electric field on greases—concentrated dispersions of soaps in mineral oils. They established that at the phase boundaries in these systems there exists an electrical double layer and that the sign and magnitude of the charges of the disperse phase and the dispersion medium can change under the action of surface-active substances and certain other factors. They observed that the particles of the disperse phase can have charges of opposite signs at the same time (electrical inhomogeneity, mosaic structure of phase boundary). If the disperse phase has charges of the same sign, then, after application of a constant field, a layer of dispersion medium forms near one of the electrodes; if the particles have charges of both signs, layers of dispersion medium are produced at both electrodes. In both cases the structural framework consisting of disperse phase particles undergoes elastic compression. At the same time the resistance of the grease to shear stress is reduced. The results of shear tests under conditions of steady flow of the grease are independent of the preliminary exposure of the latter to an electric field. Thus it was shown that the electric field induces reversible changes in the structure of greases, which in turn alter significantly their rheological properties.

We shall now review the studies of structure-formation in an electric field in suspensions of graphite and carbon black in dielectrics. It appears that the first study in this field was made by McDowell and Usher[86], who described the formation, under the action of an electric field, of chain-network structures from carbon black particles in toluene and other liquid dielectrics. The overall form of the structure-formation process in unstabilised carbon black suspensions is similar to that observed in noble metal sols[39], and therefore we shall not consider it. McDowell and Usher showed that the stabilisation of the suspension by the introduction of surface-active substances can reduce the capacity of the carbon blacks to form structures in an electric field.

Subsequently these systems were extensively studied by S. S. Voyutskii, V. A. Kargin, A. Voet, A. A. Bondi, and others†. In particular, the work of P. A. Rebinder and his school in the field of rheology and electrical properties of dispersed carbon blacks in liquid hydrocarbons must be mentioned. Voyutskii and Kargin with their coworkers[87] investigated conductimetrically the structure-formation in carbon black suspensions in a mineral oil. They believe that the observed increase of the conductivity of the system with temperature is due to an increase of the area of contact between the particles in the coagulation structures. Structure formation in graphite and carbon black suspensions in benzene, toluene, liquid paraffin, and kerosene under the action of an electric field was investigated by Yampol'skii[88]. When the structures are broken up by shaking or stirring, the mechanical strength and the electrical conductivity of the system are reduced sharply, but are gradually restored when the system is left at rest. The introduction of a surface-active substance (oleic acid, cetyl alcohol) greatly lowers the conductivity due to the growth of insulating adsorption-solvation shells on the surface of the graphite particles. Rebinder, Yampol'skii, and Wu Shu-ch'iu[89-91] investigated the behaviour of carbon black suspensions in liquid paraffin over a wide range of field strengths—from 0.025 to 500 V cm^{-1}. It was shown that the voltage-current characteristics of such systems are S-shaped: initially the conductivity of the system is constant, then it increases, and again tends to a constant value on further increase of E. These findings can be explained by a successive decrease of the thickness (breakdown) of the dispersion medium layers until at sufficiently high field strengths the thickest layers are penetrated. However, after electrical breakdown there remain extremely thin (about 10^{-7}–10^{-8} cm) residual layers of dispersion medium, which conduct current by a tunnel mechanism. Voet[92-98] and Bondi[99] hold similar views.

The combination of rheological and conductimetric studies on carbon black dispersions is of great interest. It has been established[89-91] that the stability of the structures to shear stress increases reversibly with field strength. The

† Here we are not concerned with studies of the electrical properties of carbon black dispersions in solid or highly viscous media (polymers) and in particular with the extensive series of studies on such compositions by B.A.Dogadkin, V.E.Gul', and their coworkers.

curves relating the electrical conductivity of the structured carbon black suspensions to rate of shear in an electric field are U-shaped, which can be explained by the effect of two competing factors: the decrease of conductivity due to the breakdown of the structures and its increase due to the increased frequency of collisions between the charged fragments of the carbon black chains[92-98].

This, in general, is the modern state of the problem of structure-formation in disperse systems in an electric field. In its further development the investigators will undoubtedly encounter the fundamental problem of the nature of the contact between the structural elements at various stages of structure formation. As mentioned earlier[61], the contact in stages preceding electrical breakdown (in the systems investigated by the present authors) is mainly due to forces associated with electrical polarisation, but, after typical breakdown, as in suspensions of aluminium, the particles are joined by metallic bonds (interatomic cohesion forces). However, the problem becomes complicated on going from metals to other substances, for example boron carbide: the question is whether the electrical polarisation forces at the instant of breakdown are weaker than adhesive forces or whether they are replaced by cohesive forces‡.

It is evident that very thin layers of dispersion medium between the elements of the structure always exist and their thickness depends on the lyophilicity of the disperse phase. However, as a result of the electrical breakdown, the particles are welded together and the dispersion medium layers undoubtedly disappear, but then the disperse structure ceases to be of the coagulation (reversible) type. Since before electrical breakdown many of the systems investigated exhibit appreciable conductivity, under these conditions the layers are so thin that they have little effect on the conductivity of the structure, either due to the tunnel effect or due to the breakdown of their continuity, particularly at lyophobic sites in the area of contact between the particles.

In conclusion we may note that structure formation in disperse systems in an electric field can be logically regarded as one of the aspects of the general problem of the formation of three-dimensional structures in disperse systems, which, as rightly pointed out by Rebinder, is one of the newest problems in modern colloidal chemistry. According to his classification[101-103], before breakdown the structures (at any rate those investigated by the present authors) are of the coagulation thixotropic type, but the role of electrical polarisation forces predominates. On the other hand, the structures produced after breakdown (bridges) are of the condensation (or crystallisation) type, but with the distinguishing feature that in the presence of a current the forces associated with the electric field constitute an additional stabilising factor for such structures.

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‡ The problem is closely related to the problem of electrical contact, which has been fairly thoroughly elucidated in Holme's monograph[100], for example.

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