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Dielectric Effects Produced by Solidifying Certain Organic Compounds in Electric or Magnetic Fields

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Several unexpected dielectric effects have been observed when certain organic compounds are solidified in electric or magnetic fields. When solidified in electric fields, either alternating or uni-directional, the dielectric constant of these compounds in the solid state becomes higher than normal. The increase in constant is isotropic, *i.e.*, it appears to be the same in all directions and bears no relation to the direction of the field applied during solidification. However, when the compounds are allowed to solidify in a magnetic field an anisotropic change in dielectric constant is produced causing it to be greater than normal in the direction of the applied field and lower at right angles to this direction. An explanation of the effect produced by magnetic fields is offered which is based on the diamagnetic properties and behavior of the compounds studied and their relation to dielectric properties.

Introduction

Though most polar organic compounds lose dipolar polarizability when they freeze, quite a number of compounds which retain high polarizability in the solid state are known.[1-5] In these compounds, some degree of rotational freedom of dipoles appears to persist down to temperatures well below the freezing point. It was discovered somewhat by accident that one such substance, when solidified in an electric field, showed a marked increase in dielectric constant in the solid state. Thereafter, about a dozen dielectric compounds which retain high polarizability in the solid state were solidified in electric fields and their dielectric properties studied. The constants of three compounds were found to be increased by either an alternating or a uni-directional field, a few others showed an increase when solidified in a field in the presence of paper and the remainder showed no change.

It was found too that each of the three compounds which responded to an electric field also responded to a magnetic field. When they were solidified in a magnetic field their dielectric constant in the solid state became greater than normal in the direction of the field and less than normal in a direction at right angles to this. The changes produced by both magnetic and electric fields are permanent so far as is known provided the substance is not remelted. If it is remelted and no field is applied it reverts to normal.

Experimental Method

The three dielectric compounds studied were: (1) A mixture of isomers of nitrodichloro-*o*-xylene called Nitrowax. Its composition is described by Biggs, White and Yager.[6] The principal isomers are 5-nitro-3,4-dichloro-*o*-xylene (I) and 3-nitro-4,5-dichloro-*o*-xylene (II). The melting point of the mixture is about 80°. Two different samples of Nitrowax were investigated; one prepared by the Hooker Chemical Co. is called sample A and the other prepared in this Laboratory is designated sample B. The dielectric constant of Nitrowax in the solid state is dependent upon the proportion of the principal isomers; it is found to be maximum when the composition is about 75% (I) and 25% (II). Nitrowax B is closer than Nitrowax A to this optimum composition. Consequently, while the general behavior of the two samples is similar, it will be noted in the data that the level of the constant of B is higher than A.

(2) A mixture of chlorinated naphthalenes, commercially known as Halowax, manufactured by the Bakelite Co. Its melting point is about 90°.

(3) A pure single chemical compound 3,4,5-trichloro-*o*-xylene which melts at 95°.

The dielectric constant ϵ' and dielectric loss ϵ'' of the compounds were measured in fixed capacitors with parallel, gold-plated brass electrodes. The cell was filled with molten compound and when this had solidified, capacity and conductance were measured with a capacitance bridge such as that described by Shackleton and Ferguson.[7] Repeating this procedure several times to obtain duplicate values was considered a reliable indication of the absence of voids in the dielectric.

The compounds were solidified in an electric field by applying a potential between the plates of the capacitor filled with the molten material. When the compound solidified completely, the potential was removed. In magnetic field experiments, a dielectric measuring cell filled with molten compound was kept in a magnetic field until the compound solidified completely after which it was removed from the field for measurement. In some experiments a stationary electromagnet was used and in others a permanent magnet which could be rotated was employed.

Experimental Results

Electric Fields.—The effect of solidifying a sample of Nitrowax B in a 60 cycle field of 700 v. r.m.s./m.m. is shown in Fig. 1. The dielectric constant of the material in the solid state is increased about 70% above its normal constant which is shown in the same figure. Measurements were made at one and one hundred kc./sec. The capacitance was the same at both frequencies indicating no dispersion at these frequencies. It should be noted that the transition temperature, at which ϵ' falls sharply, is the same for both states of the wax. The increase in ϵ' is dependent upon the strength and frequency of the field applied during freezing. The dielectric constant of a sample of Nitrowax A frozen in 60 cycle fields of various strengths is shown in Fig. 2. The curve appears to approach a maximum ϵ' asymptotically. Figure 3 shows the relation between the frequency of the field applied during freezing and ϵ' of a sample of Nitrowax B. The potential was kept constant in these experiments, field strength being 13 v.r.m.s./mm. ± 0.5 v. In these experiments the frequency was carried as high as the equipment at hand would permit. It would be instructive to see what would happen in fields having periods equal to or less than the relaxation time of the process. ϵ' is also increased by applying a unidirectional field, though this is less effective per volt. For example, a d.c. field of about

(1) W. A. Yager and S. O. Morgan, THIS JOURNAL, **57**, 2071 (1935).
(2) A. H. White and S. O. Morgan, *ibid.*, **57**, 2078 (1935).
(3) W. O. Baker and C. P. Smyth, *ibid.*, **60**, 1229 (1938).
(4) W. O. Baker and C. P. Smyth, *ibid.*, **61**, 2063, 2798 (1939).
(5) A. H. White, B. S. Biggs and S. O. Morgan, *ibid.*, **62**, 16 (1940).
(6) B. S. Biggs, A. W. White and W. A. Yager, U. S. Patent 2,374,973 (May 1, 1945).
(7) W. J. Shackleton and J. G. Spence, *Bell. Sys. Tech. J.*, **7**, 70 (1928).

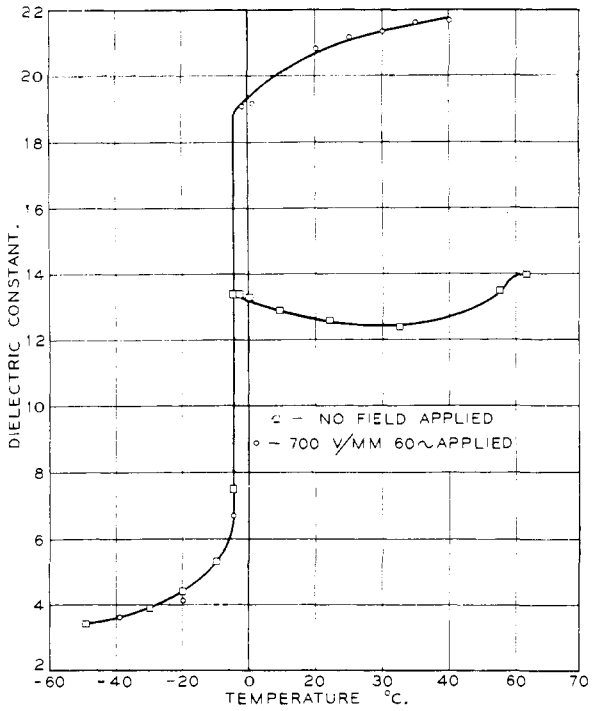

Fig. 1.—Dielectric constant of nitrowax-B at 1 and 100 kc.

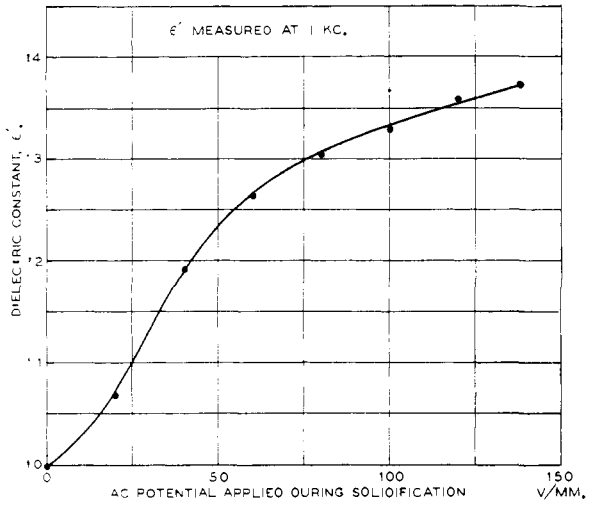

Fig. 2.—Nitrowax in fixed plate cell, 20°.

350 v./mm. will produce the same increase in the constant of Nitrowax as a 60 cycle field of 150 v./mm. This difference might be attributable to the formation of a space charge in unidirectional fields resulting in a less favorable distribution of potential throughout the volume of the dielectric than in an alternating field. To avoid the use of high fields which might cause decomposition and breakdown of the dielectric, most of our experiments have been conducted with alternating fields. However, no basic difference in behavior of the dielectric has been observed in the two types of field.

Early speculation on the mechanism of this effect led to the hypothesis that the electric field tended to align the molecules or perhaps crystallites of the wax with the axis of highest polarizability in the direction of the field. If this were so, the constant in a direction perpendicular to the field should be less than the normal value. To test this hypothesis, a dielectric measuring cell was constructed with two sets of electrodes all insulated from one another. One set consisted of coaxial tubes and the other of flat rings placed in the annular space between the tubes. The direction of the field between the rings is perpendicular to the direction of the field between the tubes. This cell was filled with Nitrowax A and ϵ' was measured using the two sets of the electrodes separately. The results were in good agreement. The wax was then melted and a 60 cycle field was applied between the rings until the wax froze. The potential was removed and the constant of the wax was measured between both the rings and the tubes. Thus, the dielectric constant was measured in the same direction as the field applied during freezing and also at right angles to that direction. Both alternating and unidirectional fields were applied during solidification. The results of these experiments are given in Table I. Here it may be seen that the dielectric constant increases in both directions and by almost the same amount.

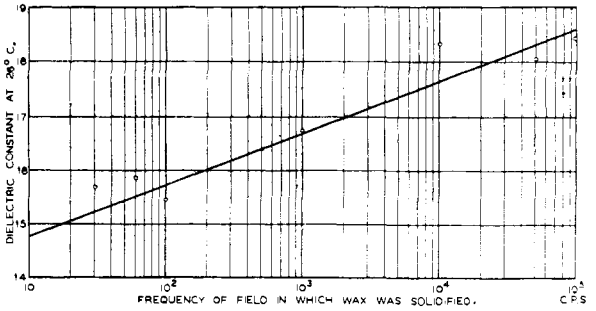

Fig. 3.—Effect of frequency on change in ϵ' of nitrowax.

TABLE I

DIELECTRIC CONSTANT OF NITROWAX-A MEASURED AT 20° AT A FREQUENCY OF 1 KC./SEC.

No field applied during solidification	
ϵ' between rings	9.1
ϵ' between tubes	9.3
60 cycle field of 10 v. r.m.s./mm. applied between rings during solidification	
ϵ' between rings	10.6
ϵ' between tubes	10.4
60 cycle field of 20 v. r.m.s./mm. applied between rings during solidification	
ϵ' between rings	11.5
ϵ' between tubes	11.0
Unidirectional field of 33 v./mm. applied between rings during solidification	
ϵ' between rings	11.9
ϵ' between tubes	11.3

The complex construction of this cell, with its possible effect on the shape of fields within it, cast some doubt on the validity of these results. To eliminate this uncertainty, another experiment was performed using a cell of very simple construction. It consisted of two metal tubes mounted coaxially

on a removable Bakelite base. The space between the tubes was filled with molten Nitrowax B and alternating potential was maintained between the tubes until the wax froze. The annulus of wax was then carefully removed and foil electrodes were attached so that ϵ' could be measured in the radial direction. These electrodes were then removed and others were attached to the annular faces in order to measure the constant at right angles to the radial direction, that is, in the longitudinal direction. The results of freezing the wax in a 60 cycle field of 14 v. r.m.s./mm. are shown in Table II. These measurements confirm the results of the previous experiment. The constant does increase essentially the same amount in both directions and this indicates that the change in dielectric constant in the solid state brought about by freezing the wax in an electric field is not related to the direction of that field. Therefore, our hypothesis was not correct. There is apparently little or no tendency for the molecules or crystallites of wax to orient during freezing through coupling of electric dipoles with the electric field.

Magnetic Fields.—A fixed-plate dielectric measuring cell filled with molten Nitrowax B was placed in a 6000 gauss field with the plane of the cell plates at right angles to the direction of the field. When the wax had solidified, the cell was removed from the field and ϵ' was measured. The constant was found to be much larger than normal as shown in Fig. 4 (curve A). The wax was remelted and the cell again placed in the magnetic field, but this time it was turned 90° from its position in the previous experiment. When the wax solidified in this position, it was found that its constant was somewhat smaller than the normal value. Point b in Fig. 4 illustrates this. Thus, in contrast with the effect of electrical fields, it appears that the effect

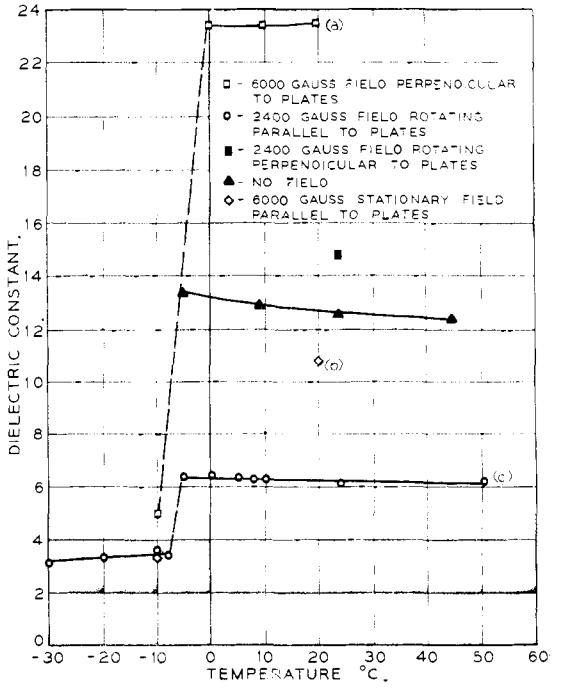

Fig. 4.—Dielectric constant of nitrowax-B at 1 and 100 kc.

TABLE II

DIELECTRIC CONSTANT OF NITROWAX-B AT 25°, 1 KC.

1.	No field applied during solidification	
	Radial direction	11.9
	Longitudinal direction	12.0
2.	60 cycle field of 140 v. r.m.s./mm. applied in radial direction during solidification	
	Radial direction	14.7
	Longitudinal direction	14.2

produced by a magnetic field is related to the direction of the field.

Discussion

The structure of the compounds which comprise Nitrowax indicates that they are diamagnetic. To rule out the presence of paramagnetic impurities, a sample of Nitrowax was examined for paramagnetic absorption but none was detected. We are, therefore, led to postulate the following mechanism of orientation of the molecules through diamagnetic coupling with the field.[8] Diamagnetic anisotropy is observed in many aromatic ring compounds and according to Selwood,[10] the principal susceptibility is generally perpendicular to the plane of the ring. Hence, in a magnetic field such molecules should tend to orient so that the plane of the rings is parallel to the field. The electric dipole will lie in the plane of the ring in these compounds because they are planar and the resultant of the electric vectors will point from the nitro and chloro groups toward the methyls. From this it is deduced that in the molecules comprising Nitrowax, the axes of the highest polarizability are perpendicular to the direction of principal diamagnetic susceptibility.

It has been shown[5,6] that the molecules of Nitrowax are able to rotate in the solid state and this permits dipolar orientation in a field. Considering the geometry of these molecules it would seem most probable that in the solid state they are able to rotate about the axis perpendicular to the plane of the ring, while rotation about any other axis would be severely restricted or absent. Therefore, when the wax is solidified in a magnetic field, these molecules would tend to orient with an axis of highest electric polarizability in the direction of the magnetic field. In any direction at right angles to this, however, the molecules will not necessarily present an axis of lowest polarizability because there is no restriction on their angular position about the axis parallel to the magnetic field. Hence, there will be only a small tendency toward lower than average polarizability in any direction at right angles to the field. This is in accord with the value of point b in Fig. 4. It follows from this that if it were physically possible to apply two discrete magnetic fields at right angles to each other to the wax during freezing then the dielectic constant of the wax should be very much lower in the third direction at right angles to the two fields. It is impossible to test this experimentally because as is

(8) A similar explanation for the behavior of liquid crystals in a magnetic field has been proposed by Carr and Spence.[9]

(9) E. F. Carr and R. D. Spence, *J. Chem. Phys.*, **22**, 1473 (1954).

(10) P. W. Selwood, "Magnetic Chemistry," Interscience Publishers, New York, N. Y., 1943.

well known two magnetic fields in the same region combine to form one. This condition can be approximated though by freezing the wax in a rotating magnetic field and then measuring its constant in the direction at right angles to the radial direction of the field. A dielectric measuring cell filled with molten Nitrowax B was placed in a magnetic field of 2400 gauss which rotated at 112 r.p.m. The plates of this cell were parallel to the magnetic field so that the direction in which the constant was measured subsequently was perpendicular to the field. When the wax had solidified, it was removed from the field and ϵ' was measured. Curve C in Fig. 4 shows the value of this over a temperature range. It is apparent that the polarizability in this direction is markedly lower than average.

The polarization of Nitrowax in these experiments may be expressed in the following approximate manner. The molar polarization of the unoriented wax, *i.e.*, soldified without a field, is

$$\frac{\epsilon' - 1}{\epsilon' + 2} F = \alpha + \frac{2B_1 + B_2}{3} \qquad (1)$$

at 20° the left side of the equation has the value

$$\frac{12.8 - 1}{12.8 + 2} F = 0.798F$$

In this expression

ϵ' = measured dielectric constant
F = a constant which includes mol. wt., density, etc.
α = that part of the polarization which is independent of the treatment of the wax during solidification

At the transition temperature −5°, all ϵ' values decrease to 3.5. This value corresponds to the polarization exclusive of orientation and α is given by

$$\alpha = \frac{3.5 - 1}{3.5 + 2} F = 0.455F \qquad (2)$$

B_1 represents dipolar polarizability along axes of highest polarizability. There are two such axes in the plane of the ring perpendicular to each other.

B_2 is the dipolar polarizability along the axis of lowest polarizability perpendicular to the plane of the ring.

When the wax is solidified in a strong stationary magnetic field, the orientation in the direction of the field corresponds to B_1 type polarizability.

$$\frac{23.5 - 1}{23.5 + 2} F = \alpha + B_1 = 0.883F \qquad (3)$$

$$B_1 = 0.428F$$

From (1), (2) and (3)

$$\frac{2B_1 + B_2}{3} = 0.343F$$

and

$$B_2 = 0.173F$$

Thence the calculated dielectric constant for polarization of Type B_2 is $\epsilon' = 6.06$.

This result corresponds closely to the constant of the wax solidified in the rotating field of 2400 gauss and measured perpendicular to the field. Moreover, when the substance is solidified in the stationary magnetic field, its polarizability at right angles to the direction of the field should be the average of B_1 and B_2

$$\frac{\epsilon' - 1}{\epsilon' + 2} F = \alpha + \frac{B_1 + B_2}{2} \qquad (4)$$

$$\epsilon' = 10.25$$

in fair agreement with the measured value 10.85.

The tangent of the loss angle of Nitrowax B solidified in various fields is shown in Fig. 5. It may be seen that with one exception, a change in dielectric constant is accompanied by a proportionate change in dielectric loss. The exception is the case where the wax was solidified in a stationary magnetic field and measured in the direction of that field. This treatment produced an increase in constant but loss remained essentially the same as that of the wax solidified without the field.

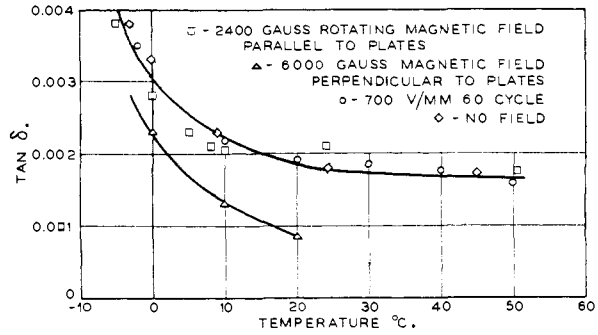

Fig. 5.—Tangent of loss angle of nitrowax-B at 1 kc.

The results of solidifying Nitrowax in a rotating magnetic field and alternating electric field at the same time are shown in Fig. 6. In this experiment the strength of the magnetic field was kept constant at 2400 gauss and the electric field was varied. The direction of the electric field is normal to that of the magnetic field and ϵ' was measured in the direction of the electric field. The magnetic field tends to decrease the constant in the direction measured and it is counteracted by the electric field. When the electric field reaches about 33 v./mm. the constant of the wax is the same as though no field were present.

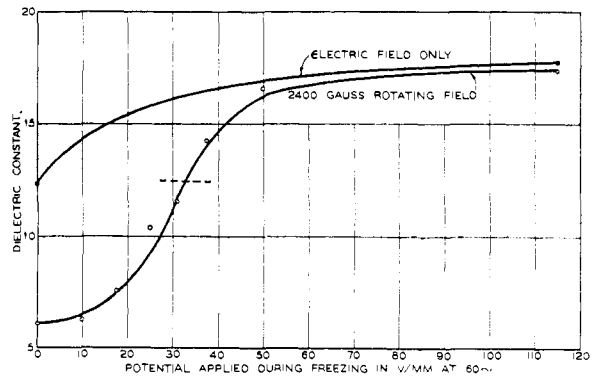

Fig. 6.—Dielectric constant at 26° at 1 kc. and 100 kc.

The dielectric constant of Halowax 1001 can be increased in the solid state about 15% by solidifying it in a 60 cycle field of 625 v./mm. It is reduced about 10% when solidified in a rotating magnetic field of 2400 gauss and measured at right angles to the direction of the field. The dielectric constants of 3,4,5-trichloro-*o*-xylene solidified in an electric field, solidified without a field and solidified in a rotating magnetic field are shown in Fig. 7. In the last case the ϵ' is measured at right angles to

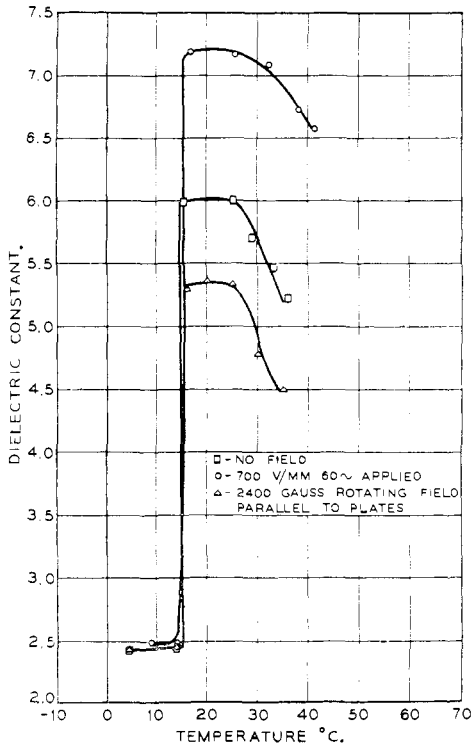

Fig. 7.—Dielectric constant of 3,4,5-trichloro-*o*-xylene at 1, 10 and 100 kc.

the plane of the rotating field. This compound undergoes a transition at 15° and again as with Nitrowax the manner in which it was solidified does not alter this. It would seem improbable, therefore, that the material solidified in the field is different in crystalline form from that solidified without a field.

Besides these dielectric compounds described above, some others have been observed to undergo a change when solidified in an electric field in the presence of paper. For example, the capacity of paper capacitors impregnated with hydrogenated castor oil may be increased about 10% by allowing the impregnant to solidify in a 60 cycle field of 115 v., despite the fact the hydrogenated castor oil alone in a fixed plate cell is unaffected by application of an electric field during freezing.

It may be of interest to note some of the compounds examined which do not show any change in ϵ' when solidified in fields. Paraffin wax, a nonpolar material, shows no difference in ϵ' whether solidified in a field or without a field. Carnauba wax which forms stable and long-enduring electrets shows no change in ϵ' in the solid state when allowed to freeze in fields. Both unidirectional and alternating electric fields were employed. Succinonitrile, a compound having extremely high polarizability in the solid state undergoes no apparent change when solidified in a field and similarly tetrachloro-*m*-fluorotoluene which displays anomalous dispersion in the solid state shows no response.

Summary and Conclusions

It has been demonstrated that the solid state dielectric constant of several organic compounds is increased isotropically when they are solidified in an electric field. When these compounds are solidified in a magnetic field their constant is increased in the direction of the field and decreased at right angles to this. These effects have been studied quite exhaustively in a dielectric compound known as Nitrowax. Subjecting this compound in the liquid state to a field does not alter its dielectric constant. Likewise, applying a field after the compound has solidified causes no change. It appears that fields affect the compound only during the transition from liquid to solid. No significant difference is apparent under the microscope in Nitrowax whether solidified in electric or magnetic fields or without a field. Also, no difference in the density of the material has been detected. Nitrowax and 3,4,5-trichloro-*o*-xylene undergo a transition in the solid state and it is found that the temperature at which the transition occurs is the same whether the compounds were or were not solidified in fields. All of this indicates that no fundamental morphological change is brought about by solidifying these materials in electric or magnetic fields. The effect of magnetic fields may be adequately explained by diamagnetic coupling of the molecules with the field during solidification. No satisfactory explanation for the effect of electric fields has been developed thus far. The isotropic increase in constant suggests that direct coupling of electric dipoles with the fields is not in itself sufficient. However, one may speculate that the molecules aggregate in domains which are randomly disposed. An electric field may in some manner cause the molecules within a domain to orient with respect to one another so as to increase through mutual interaction the polarizability of the domain beyond the sum of the polarizabilities of the individual molecules which comprise it. Thus the dielectric constant of the mass would increase without relation to the direction of the electric field applied during solidification.

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