

Electrical Properties of Some Newly Prepared Insulating Greases

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ABSTRACT: Different samples of poly(vinyl chloride) (PVC) greases were formulated from PVC, triisopropylphenylphosphate plasticizer (TIPPP), and a wax gel (microcrystalline wax and transformer oil) system, together with variable proportions of phenol formaldehyde, stearyl phenol formaldehyde, or stearyl phenol formaldehyde urethane resins. The effect of resin structure on the electrical properties (dielectric constant, dielectric loss, and conductivity) of the PVC–TIPPP–wax gel system was studied to obtain a plasticized PVC grease of high electrical insulation and fire-retarding characters. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 68: 699–708, 1998

Key words: poly(vinyl chloride); dielectric properties; electrical insulation; fire resistance

INTRODUCTION

Until comparatively recently, individual greases were required for specific purposes. However, with the advent of new types of formulations, a wide range of applications is now covered. This has resulted in the emergence of multipurpose industrial greases, which are replacing the very numerous specialized materials formerly required. Greases are products composed of a liquid phase (mineral and synthetic oils) and a thickening phase. The known greases used in insulator service are classified on the basis of their formulations into hydrocarbon type (thickened by paraffins, petrolatum, and ceresin), polymer type (thickened by high molecular compounds), and silicone type.^{1–6}

The aim of this study is to investigate systematically the effect of adding increasing quantities

of phenol formaldehyde, synthesized stearyl phenol formaldehyde, or stearyl phenol formaldehyde urethane resins on the electrical properties of the poly(vinyl chloride) (PVC), triisopropylphenylphosphate (TIPPP), and wax gel (transformer oil and microcrystalline wax) system in an attempt to improve these properties and obtain a good grease for high-voltage insulation purposes.

EXPERIMENTAL

Materials

1. PVC, was used with a K-value of 70, an apparent bulk density of 0.30 g/mL, and a viscosity number of 125 g/mL.
2. Transformer oil was used with a viscosity of 12.5 C.st. at 100°F, a pour point of 70°F, and a dielectric strength of 30 KV.
3. Microcrystalline wax was used with a melting range of 78–81°C, and an average number of carbon atoms of C₄₅–C₅₀.

All electrical measurements were done in the NRC by Azima L. G. Saad.

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Table I Specifications of Stearyl Phenol Formaldehyde Resin

Specification	Result
Specific gravity at 20°C	1.25
Softening point (°C)	77
Water absorption (%) 24 h at 25°C	1.82

Synthesis of Stearyl Phenol Formaldehyde Resin

A solution of stearyl phenol⁷ in toluene, formalin (40%), and hydrochloric acid (33%) as a catalyst were slowly heated to 95°C while the exothermic reaction was progressed. After refluxing for 1.5 h at 95°C, the amount of water formed was removed. After cooling to 5°C, the resin was washed with water, then the toluene was distilled off to obtain the required resin. The specifications of stearyl phenol formaldehyde resin are shown in Table I. The reaction can be illustrated in Scheme I.

Synthesis of Stearyl Phenol Formaldehyde Urethane Resin

Toluene diisocyanate (42.7 g) dissolved in a toluene-xylene mixture of 1 : 1 (42.7 g) was heated to 115°C for 0.5 h. Then, the stearyl phenol formaldehyde resin (35.5 g) was mixed with the resulting mixture under reflux, followed by addition of triethylamine as a catalyst (6% based on the stearyl phenol formaldehyde resin) for 1.5 h at 130–140°C to give the required stearyl phenol formaldehyde urethane resin. The specifications of stearyl phenol formaldehyde urethane are

Table II Specifications of Stearyl Phenol Formaldehyde Urethane Resin

Specification	Result
Dielectric constant, 60 cycles	3.0
Power factor, 60 cycles	0.0026
Loss factor	0.0078
Water absorption (%) 24 h at 25°C	0.054
Appearance	Reddish brown, opaque semisolid

given in Table II. The reaction can be illustrated in Scheme 2.⁸

The structure of stearyl phenol formaldehyde urethane was confirmed from its infrared (IR) spectrum, measured by an Fourier transform IR (FTIR) spectrometer at wave numbers from 4000 to 500 cm^{-1} and a transmittance percentage from 20–80 (Fig. 1), which shows peaks at 3380, 3060, 2924, and 1716 cm^{-1} that correspond to NH, CH aromatic, CH_2 and $\text{C}=\text{O}$ groups, respectively.

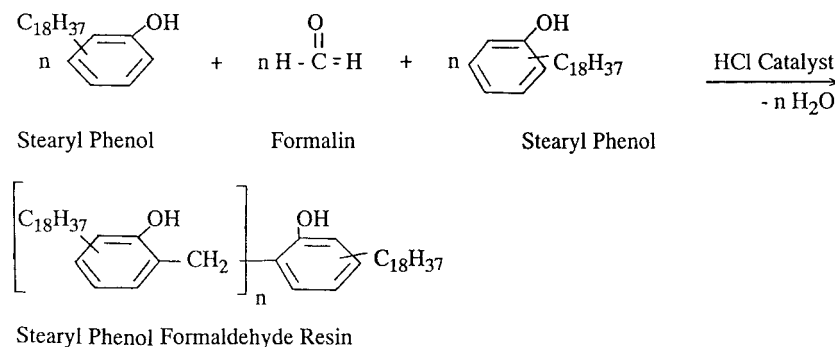
Formulations of the Samples

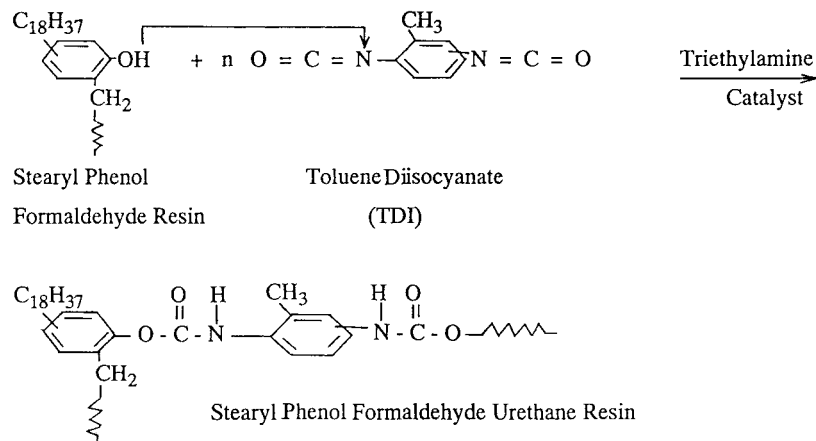
Preparation of Wax Gel

The transformer oil (1.5 parts) was heated to 70–80°C, and the microcrystalline wax (1 part) was added portion-wise under stirring for 0.25 h. After cooling, the mixture was thickened to a gel.

In the present work, several formulations were obtained by mixing the components in the proportions shown in Table III. The general procedure for formulation is described as follows.

Homogeneous samples (greases) were prepared by adding variable proportions of phenol formaldehyde, synthesized stearyl phenol form-

**Scheme 1**



Scheme 2

aldehyde, or stearyl phenol formaldehyde urethane resins portion-wise at room temperature to a composition containing 10 g PVC, 4 g TIPPP, and 2.5 g wax gel (1.5 g transformer oil and 1 g microcrystalline wax) under stirring. The obtained samples are denoted by D₀, D₁, and D₂–D₁₂. The specifications of the resulted greases are given in Table IV.

It is significant to point out that the ratios of the polymer, plasticizer, wax gel, and resin used in the formulations of the prepared greases proved to be the best since other attempts to mix these ingredients in other ratios failed to produce good quality greases. Higher ratios of wax hardened the greases, whereas higher amounts of oil defected them (caused oil bleeding and lowering of sliding temperature and viscosity). Moreover, higher ratios of resin or polymer led to a decrease in the cohesive force of the components, for instance, separation of the polymer or resin from the grease.

Dielectric Measurements

Permittivity ϵ' and dielectric loss ϵ'' for the denoted samples were measured at different frequencies ranging from 100 Hz to 100 kHz. An LCR meter type AG-4311B Ando electric LTD with the test cell NFM/5T was used. The capacitance C and the loss tangent ($\tan \delta$) were obtained directly from the bridge, from which ϵ' and ϵ'' were calculated. The samples were in the form of discs of 58 mm in diameter and of 3 mm in thickness. Calibration of the apparatus was carried out using standard samples (Trolitul, glass, and air) of thicknesses of 3 mm; the accuracy for ϵ' was $\pm 1\%$ and $\pm 2\%$ for ϵ'' . The measurements were carried

out at temperatures 20, 30, and 40°C using an ultrathermostat.

Conductivity Measurements

The electrical conductivity (σ) of the investigated samples was measured by the application of Ohm's law using the test cell NFM/5T. A power supply unit GM 45161/01 from Philips, (Netherlands) was used. The potential difference V between the plates holding the sample and the current I flowing through it was measured by a multimeter type URI 1050 from Rohde and Schwarz (Germany). The electrical conductivity is calculated using the following equation:

$$\sigma = \frac{dI}{AV} \text{ mho m}^{-1}$$

where d is the thickness of the sample in m, and A is its surface area in m².

RESULTS AND DISCUSSION

Polymers such as PVC are known to have kinetically rigid chains. On the addition of low molecular admixtures, particularly, polar plasticizers, they are effective enough to penetrate inside the molecular bundles of PVC and to separate the polymeric chains. Accordingly, the mutual interaction between plasticizer and PVC becomes appreciable, leading to aggregates or segments having sizes smaller than that of PVC, that is, segments of higher molecular mobility. Since the appearance of dipole segments and dipole groups

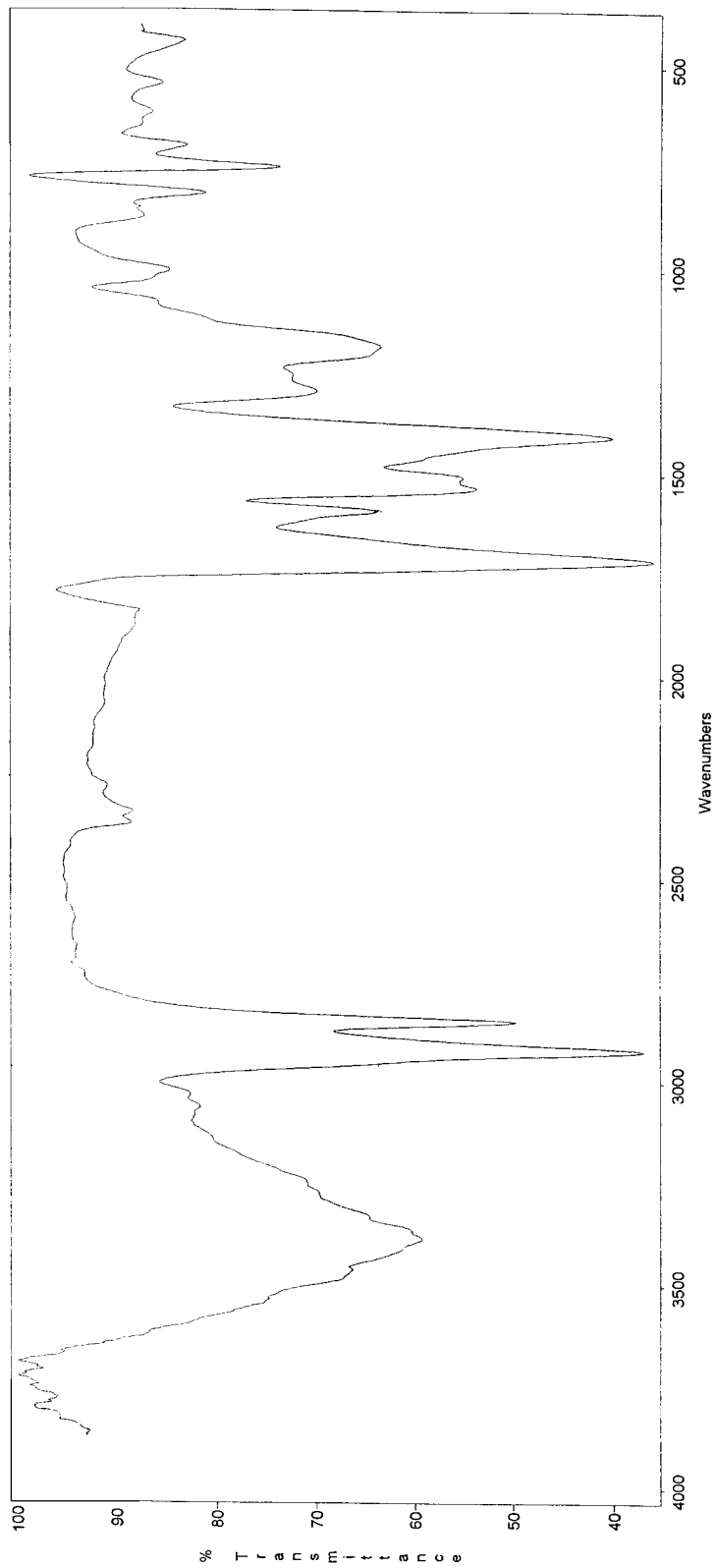


Figure 1. IR spectrum of stearyl phenol formaldehyde urethane resin.

Table III Formulations of the Samples

Constituents and Parts by Weight (g)	Sample Notation												
	D_0	D_1	D_2	D_3	D_4	D_5	D_6	D_7	D_8	D_9	D_{10}	D_{11}	D_{12}
Poly(vinyl chloride) (PVC)	10	10	10	10	10	10	10	10	10	10	10	10	10
Triisopropylphenylphosphate (TIPPP)	4	4	4	4	4	4	4	4	4	4	4	4	4
Wax gel	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5
Phenol formaldehyde	—	1.25	2.5	3.75	5	—	—	—	—	—	—	—	—
Stearyl phenol formaldehyde	—	—	—	—	—	1.25	2.5	3.75	5	—	—	—	—
Stearyl phenol formaldehyde urethane	—	—	—	—	—	—	—	—	—	1.25	2.5	3.75	5

Table IV Specifications of Greases

Specifications	Sample Notation	
	D_0	$D_1D_2D_3D_4$ $D_5D_6D_7D_8$ $D_9D_{10}D_{11}D_{12}$
Sliding temperature (°C)	72–86	95–110
Behavior at high temperatures (180–190°C)	Gelation	Gelation
Fire-retarding ⁽⁶⁾	Nonburning	Nonburning
External appearance	Semisolid transparent	Semisolid opaque
Ease of removal-(toluene : xylene, 1 : 1)	Good	Good

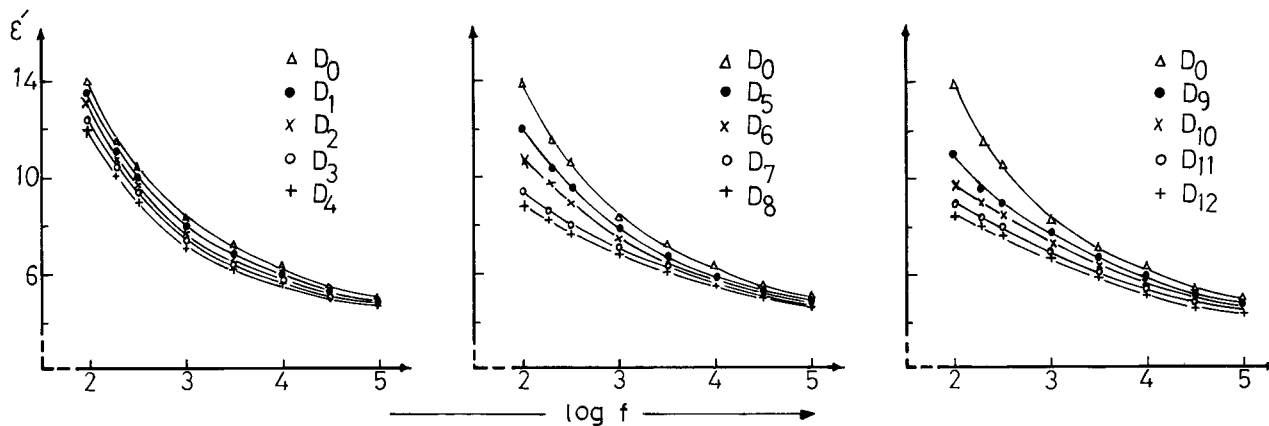


Figure 2 The permittivity (ϵ') versus frequency at 20°C for the PVC-TIPPP-wax gel system mixed with variable proportions of phenol formaldehyde, stearyl phenol formaldehyde, and stearyl phenol formaldehyde urethane (D_0 , D_1 , D_2 , and D_3 - D_{12}); see Table III.

in polymers is associated with the mobility of the kinetic units of the macromolecular chain, therefore, plasticized PVC should exhibit higher mobilities.¹⁰

In this investigation, the treatment of PVC with admixture consisting of TIPPP and wax gel (microcrystalline wax and transformer oil) produces a PVC-TIPPP-wax gel system (sample D_0) that is found to have some electrical properties. In an attempt to improve the electrical properties of sample D_0 and directing it to be a high electrical insulator, phenol formaldehyde, stearyl phenol formaldehyde, or stearyl phenol formaldehyde urethane are formulated together in different concentrations (Table III). The permittivity (ϵ') and dielectric loss (ϵ'') for the prepared samples (D_0 , D_1 , and D_2 - D_{12}) were studied over the frequency region from 100 Hz to 100 kHz at 20°C.

It is evident from Figure 2, which represents the variation of ϵ' with frequency at 20°C, that the value of ϵ' decreases with increasing frequency, which may be due to dielectric dispersion. Moreover, Figure 2, as well as Figure 3, which represents the relation between ϵ' and the content of the investigated additives at frequencies of 100 Hz, 1 kHz, and 100 kHz show that the value of ϵ' decreases with increasing the content of each additive in the sequence: phenol formaldehyde > stearyl phenol formaldehyde > stearyl phenol formaldehyde urethane, especially at the very low-frequency region. This could be attributed to steric hindrance due to the presence of large radicals in these additives, which increases in the same sequence, despite the presence of a number of polar groups that are capable of orientation in

an electric field. This restricts the rotation of the large molecules, and, accordingly, the decrease of ϵ' is more pronounced when stearyl phenol formaldehyde urethane is introduced (samples D_9 , D_{10} , D_{11} , and D_{12}) and reaches 6.6 and 6.8 at 1 kHz for samples D_{11} and D_{12} , respectively. These results are in agreement with the data of standard plasticized PVC insulated wire¹¹ ($\epsilon' = 5-7$ at 1 kHz and 25°C) and supported by the results of plasticized PVC systems^{11,12} ($\epsilon' = 4.5-6.5$ at 1 kHz and 20°C).

It is apparent from Figure 4, which represents the variation of ϵ'' with frequency at 20°C, that the value of ϵ'' in the lower-frequency region decreases with increase in the content of each additive in the following sequence: phenol formaldehyde > stearyl phenol formaldehyde > stearyl phenol formaldehyde urethane. From Figure 4, it is clear that for samples D_4 , D_7 , and D_{10} , there is an absorption region with a maximum at about 300 Hz. Also, for samples D_8 , D_{11} , and D_{12} , the curves are broad, indicating an overlapping of more than one absorption region. In addition, a tail of high-frequency absorption region with a maximum at a frequency higher than 100 kHz appears and becomes more pronounced for sample D_0 and is associated with the pure Debye losses due to dipole orientations caused by movements of the main backbone carbon. The value of ϵ'' reaches 0.3 and 0.4 at 1 kHz for samples D_{11} and D_{12} , respectively. Similar results have been found in Tager¹⁰ ($\epsilon'' = 0.35-0.6$ at 1 kHz and 25°C) and Bishai et al.¹² and Saad et al.¹³ ($\epsilon'' = 0.35-0.7$ at 1 kHz and 20°C). The decrease in the ϵ'' value may be due to the presence of very bulky substitu-

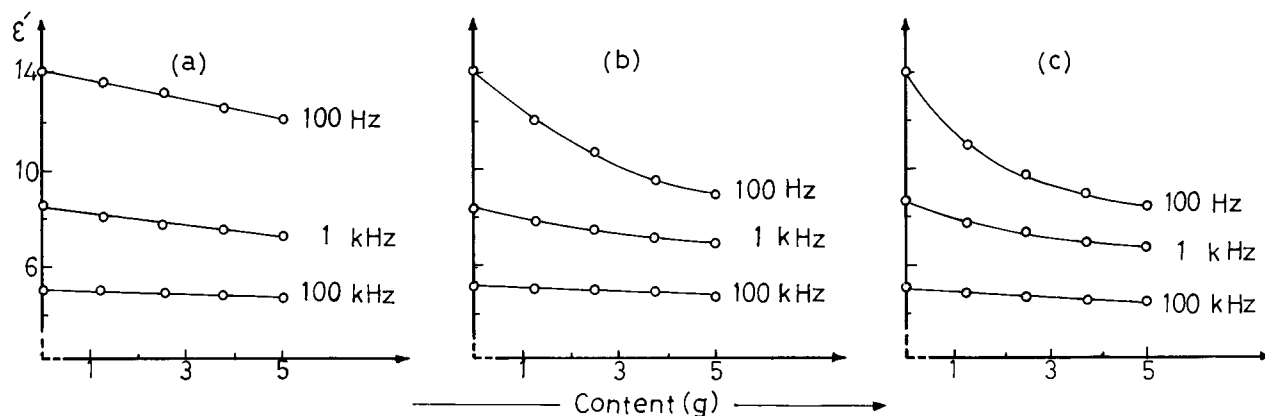


Figure 3 The relation between permittivity (ϵ') and the content of phenol formaldehyde (a), stearyl phenol formaldehyde (b), and stearyl phenol formaldehyde urethane (c) at frequencies 100 Hz, 1 kHz, and 100 kHz.

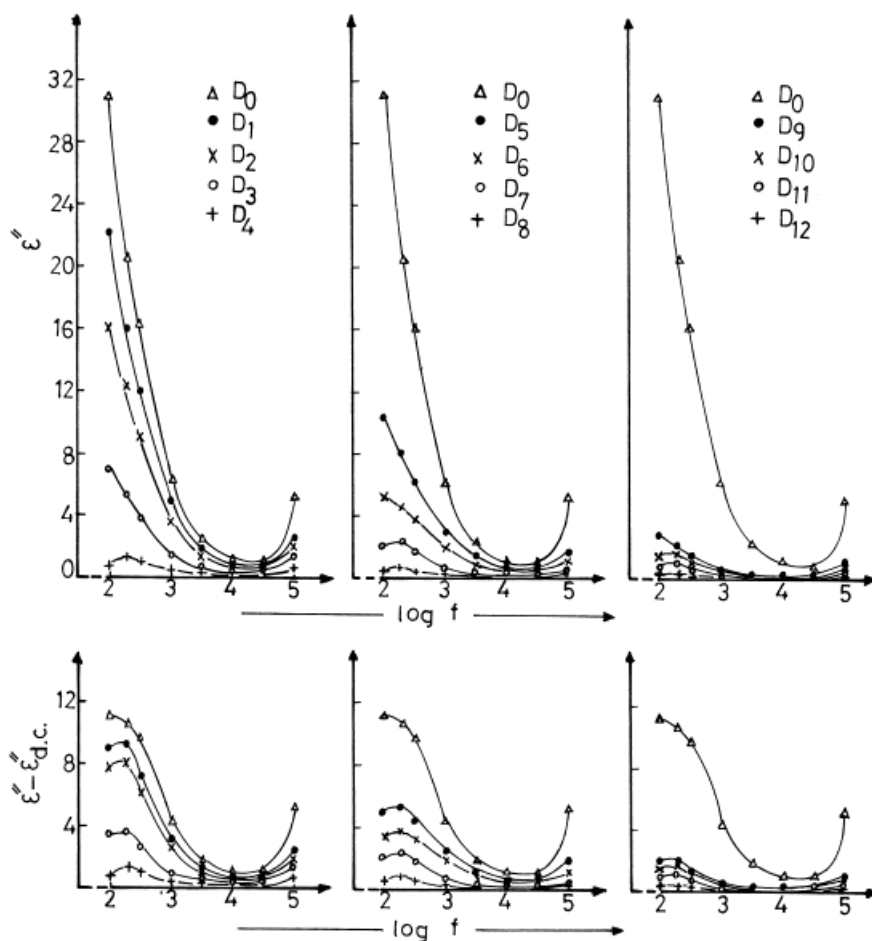


Figure 4 The dielectric loss (ϵ'') and $\epsilon'' - \epsilon''_{dc}$ versus frequency at 20°C for the PVC-TIPPP-wax gel system mixed with variable proportions of phenol formaldehyde, stearyl phenol formaldehyde, and stearyl phenol formaldehyde urethane (D_0 , D_1 , D_2 , and D_3 - D_{12}); see Table III.

ents in these additives, which reduces the molecular mobility.

The low-frequency losses may be due to either direct current (dc) conductivity,^{14,15} resulting from the increase of ion mobility or the Maxwell–Wagner effect¹⁶ as a result of an alternating current (ac) in phase with the applied potential, or to both. To confirm this, the dc conductivities of the investigated samples were measured by application of Ohm's law to the dc flowing through the samples at 200 V and at temperatures from 20 to 50°C. All investigated samples showed appreciable dc conductivity. The dielectric losses due to the dc conductivity (σ) at the different frequencies (ω) are calculated using the following equation.¹⁷

$$\varepsilon''_{dc} = \frac{9 \times 10^{11} 4\pi\sigma}{\omega}$$

and subtracted from the values of ε'' in the low-frequency region. The data of ε'' after subtracting ε''_{dc} are plotted versus $\log f$ and represented in Figure 4. From this figure, it is clear that for sample D₀, there is an absorption region extending below 100 Hz that may be due to rotation of large aggregates of the chain. Unfortunately, we cannot give further interpretation of this region since we have no measurements below 100 Hz. With respect to sample D₀ mixed with phenol formaldehyde (samples D₁, D₂, D₃, and D₄), stearyl phenol formaldehyde (samples D₅, D₆, and D₇) and stearyl phenol formaldehyde urethane (samples D₉ and D₁₀), there is an absorption region with a

maximum at about 300 Hz, which decreases with increasing the concentration of each additive.

It may be concluded that the low-frequency losses are not totally dc losses and that they may comprise Maxwell–Wagner losses, as the difference between the permittivities of the different ingredients in the investigated samples are relatively large.

On the other hand, the change of the electrical conductivity (σ) of samples D₀, D₁, D₂, and D₃–D₁₂ with temperature is shown in Figure 5. It is evident from this figure that, at lower temperatures, σ of these samples is low and increases as the temperature is increased. This may be due to the increase of the mobility of the ionic bodies that takes place as a result of the excitation by heat, leading to an increase in the conductivity of the investigated samples. Figure 5 also shows a pronounced increase in σ of sample D₀ with increasing temperature. This may be attributed to the rupture of the double bonds (the π bonds) due to the excitation by heat with the formation of free electrons that are mobile under the influence of an electric field and thus greatly increase the degree of electrical conductivity in this sample. At the higher temperatures, it is also probable that hydrogen chloride is evolved from PVC and that the chlorine ions are free to follow the external field. With respect to sample D₀ mixed with phenol formaldehyde (samples D₁, D₂, D₃, and D₄), stearyl phenol formaldehyde (samples D₅, D₆, D₇, and D₈), or stearyl phenol formaldehyde urethane (samples D₉, D₁₀, D₁₁, and D₁₂), Figure 5 also

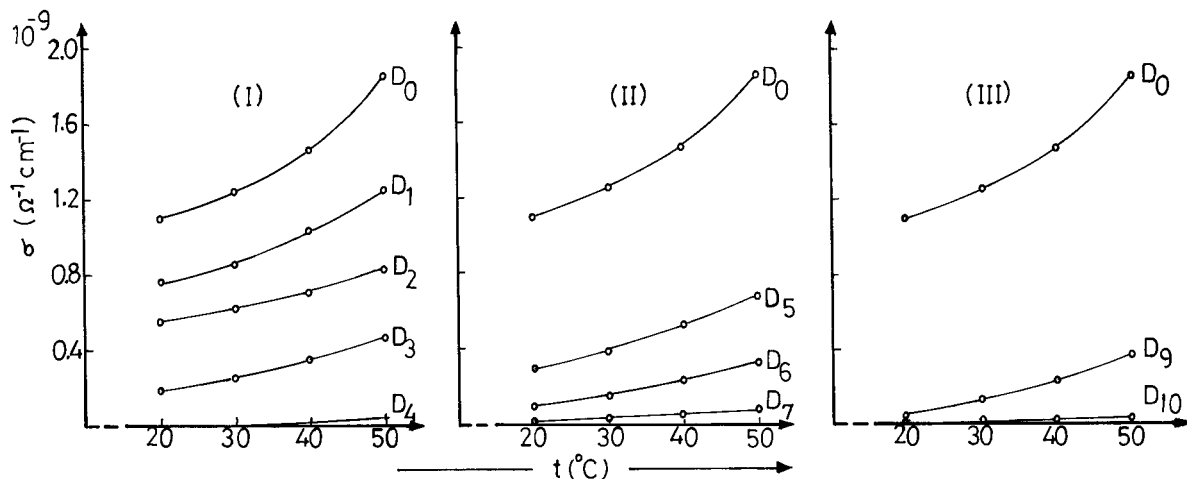


Figure 5 The relation between conductivity (σ) and temperature (t) for samples D₀, D₁, D₂, D₃, and D₄ (I), samples D₀, D₅, D₆, and D₇ (II), and samples D₀, D₉, and D₁₀ (III).

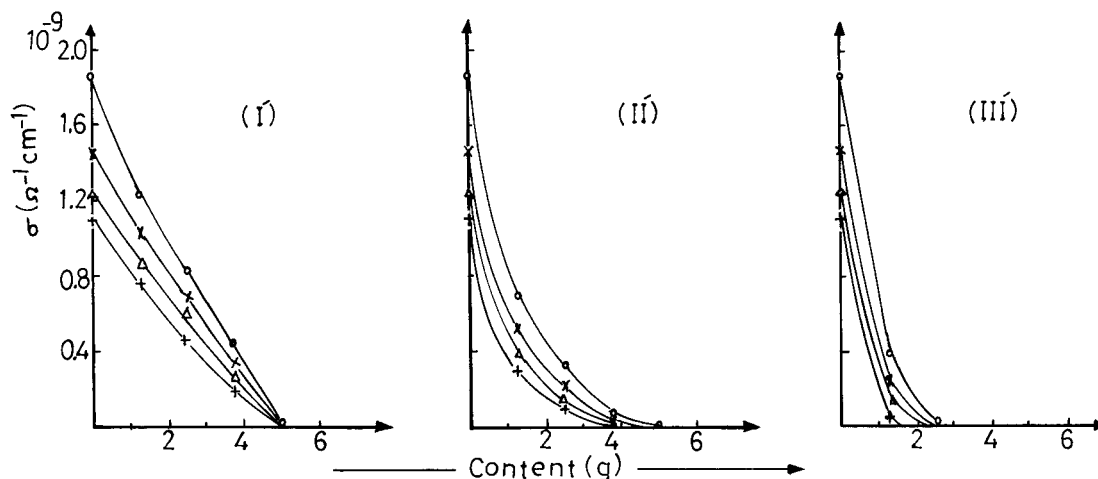


Figure 6 The relation between conductivity (σ) and the content of phenol formaldehyde (I'), stearyl phenol formaldehyde (II'), or stearyl phenol formaldehyde urethane (III') at the following different temperatures: (+) 20, (Δ) 30, (X) 40, and (O) 50°C.

shows that the value of σ decreases with increase in the content of each additive in the following sequence: phenol formaldehyde > stearyl phenol formaldehyde > stearyl phenol formaldehyde urethane, especially at higher temperatures. This may be attributed to steric hindrance due to the presence of the large radicals that plays a great role in decreasing the mobility of the electric charges, and, accordingly, the conductivity of these samples decreases. It reaches no value for samples D₈, D₁₁, and D₁₂ (having 5 g of stearyl phenol formaldehyde, and 3.75 and 5 g of stearyl phenol formaldehyde urethane, respectively). Figure 6 shows the relation between conductivity (σ) and the content of each additive at temperatures from 20 to 50°C.

CONCLUSIONS

The prepared PVC greases proved to be more available than the other greases for the following reasons.

1. The constitution of samples proved to be stable at high temperatures.
2. These samples are not hard and melt without separation of their components.
3. From the fire-retardant experiments, it is evident that these greases are difficult to burn due to the presence of the TIPPP plasticizer and the resin.
4. The chief point of the difference between the

types of greases is the type of resin used as an ingredient of the greases.

5. The electrical conductivity of a prepared sample having 10 g PVC, 4 g TIPPP, and 2.5 g wax gel is decreased by the addition of the investigated additives in the following sequence: phenol formaldehyde > stearyl phenol formaldehyde > stearyl phenol formaldehyde urethane. It reaches no value for samples having 5 g of stearyl phenol formaldehyde, and 3.75 and 5 g of stearyl phenol formaldehyde urethane (samples D₈, D₁₁, and D₁₂, respectively), making it of great interest as a good grease for high-voltage insulation purposes.

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