The Hydrophilicity of Some Lacquers for Electrical Use

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Abstract. Through gravimetric determinations, volume resistivity, dielectric spectroscopy, and comparative thermal analysis (TG, DTA and DTG), the interactions between the distilled water and three different types of alkyd-epoxy-melamine, epoxy and polyurethane lacquers were studied. From the experimental determinations it was found that after 700 h of immersion in water at 20 ± 2°C the alkyd-epoxy-melamine based lacquer has a maximum water uptake, respectively 1.76%, followed by the epoxy lacquer 1.4% and polyurethane 0.93%. The thermal analysis suggests that because the water retained by the investigated polymers does not change the TG diagrams in the temperature range up to 150 °C, which suggests that the weight increase of the samples during the immersion could be due to some chemical processes between the water and polymer by which the chemistry structure of the polymer changes. Through electrical measurementes one can observe that after the immersion in water (over 700 hours), dielectric loss increases and the volume resistivity (measured in DC) of the investigated lacquers decreases, which is explained by the increasing of polar groups (–OH) in the polymer structure. A comparative analysis of the experimental data reveals that in electrical applications the lacquer LS (polyurethane) is superior to the lacquers L-528 (alkyd-epoxy-melamine) and LG (epoxy), because it has no mass losses (structural changes) up to 280°C it has a volume resistivity of about 21 % higher than L-G, and about 300 % higher than L-528, and has water uptake and dielectric loss substantially lower comparing to L-528 and L-G.

Keywords: lacquer for electrical use, water uptake, dielectric loss, volume resistivity, thermal analysis, water treeing

1.Introduction
In the perspective of the sustainable development, the durability and safety in exploitation of electrical equipments represents a priority issue.

The durability and safety in exploitation of an electrical equipment are mainly determined by the electrical insulating materials that enter in their construction [1, 2].

The electro-insulating materials under the stress factors action (thermal, electrical, chemical, microbiological, etc.) specific to the operating environment [3-8] undergo a series of changes, as a result of which the functional characteristics are degraded, the material is ageing, leading to the failure of electrical appliances and equipment.

Various polymers are frequently used in electrical applications, both to ensure an adequate level of insulation and to perform anti-corrosion protection layers and / or to strengthen magnetic core and windings of electric transformers and / or motors [9], etc.

In these applications, the hydrophilicity of the polymers, respectively their water absorption capacity can be decisive both in the insulation water treeing initiation and in the deterioration of the mechanical, dielectric and anticorrosive characteristics of the protection and / or consolidation layers.

It is noted that the stressors factor specific to the exploitation environment act synergistically leading to an accelerated ageing of the polymeric materials used in electrical applications. Humidity,
including water absorbed due to the hydrophilic process, favours the formation and growth of microbial colonies, which leads to biodeterioration of polymers [3, 4, 10-13] and metal components corrosion [4-8]. On the other hand, by exposure in the extremely low frequency electric field especially at the industrial frequency of 50Hz, the growth and multiplication of microorganisms (especially moulds [15-18]) is stimulated as consequence an accelerated biodeterioration of polymers [19, 20] and metal components corrosion [21-24]. The electrical stress acting on the polymeric insulations is intensified by the harmonic components of the 50 Hz industrial frequency primarily generated by the reactive consumers [25-28], a situation when, in the presence of humidity, the initiation and growth of the water tree in the polymeric insulation is greatly accelerated [29].

A particular case is represented by the situations in which the lacquer the polymer for electrical use, specific to the application is in contact with electroinsulating fluids (such as oil of transformer) with a given humidity content [30-37]. At the same time, the water absorption of polymers can be determined by modifying the dielectric characteristics of composite materials based on polymers with various fillers [38-45].

Taking into consideration all these aspects, the presents an experimental study on the water absorption of some lacquers for electrical use on their dielectric performances.

2. Materials and methods

In order to evaluate the behaviour of some lacquers for electrical use in prolonged contact with water, films with a thickness of 30 ± 5μm were prepared from three different types of lacquers (commercial products) based on alkyd-epoxy-melamine, epoxy polymer and polyurethane.

The provenance and structure of the lacquers used are presented in Table 1.

<table>
<thead>
<tr>
<th>Sample Cod</th>
<th>Type of lacquer</th>
<th>Structure</th>
<th>Solvent</th>
</tr>
</thead>
<tbody>
<tr>
<td>L - 528</td>
<td>528 EZ [46]</td>
<td>monocomponent alkyd-epoxy-melamine</td>
<td>Thinner 528 EZ - a mixture of aromatic hydrocarbons and alcohols</td>
</tr>
<tr>
<td>L - G</td>
<td>ROPOXID 501 [47]</td>
<td>bicomponent - epoxy</td>
<td>Acetone</td>
</tr>
<tr>
<td>L - S</td>
<td>SIGMADUR™ CLEARCOAT [48]</td>
<td>bicomponent - polyurethane</td>
<td>Thinner 21-06 a mixture of aromatic hydrocarbons and alcohols</td>
</tr>
</tbody>
</table>

The lacquer samples, foils with determined area, were immersed in distilled water and stored for 720 h at a temperature of 20 ± 2 °C. Water absorption was determined gravimetrically by periodic weighing with a PRECISA EP 125SM digital analytical balance. The dielectric characteristics evolution during immersion in distilled water of the investigated lacquer samples was evidenced by the dielectric spectroscopy technique, respectively the dielectric loss measurement, $\tan\delta$ with specialized equipment AMTEK - 1296 Dielectric interface - Solartron Analytical. Based on the insulation resistance values measured at ambient temperature (20 ± 2 °C) with a FLUKE 1550B MegOhmMeter (in DC, at 250 V), the volume resistances $\rho$ [9] of the lacquers investigated before and periodically after their immersion in water were calculated. Determinations of $\tan\delta$ and $\rho$ were performed on lacquer samples extracted from water and dried by storage for 30 min in air at 20 ± 2 °C.

In order to highlight the possible structural changes undergone by the lacquers investigated during the immersion in water, the characteristics of TG, GTA and DTG curves were recorded using coupled thermal analysis techniques for the initial samples and for those maintained for 720 hours in water.

Thermal analysis determinations were performed in synthetic air (10 mL / minute) at a gradient of 10K / minute with specialized equipment.

TG/ DTG+DTA analyzer produced by Netzsch-Germany. The mass of each sample was around 15 mg. The results of measurements were processed and graphically represented using the dedicated Proteus Software, from Netzsch-Germany.

The thermal analysis determinations were performed on the lacquer samples extracted from water and dried by storage for 24 h in air at 20 ± 2 °C.
3. Results and discussions

The water uptake (WU) of the investigated lacquers was determined by the initial weighing \((m_0)\) and at different exposure times \((m_t)\) of the samples. For the calculation of WU, expressed in % the relation (1) was used:

\[
WU[\%] = 100 \cdot \frac{m_t - m_0}{m_0}
\]  

(1)

The time evolutions of WU by immersion in distilled water at 20 ± 2 °C of the investigated lacquer samples are shown comparatively in Figure 1.

Analyzing Figure 1, it is observed that, in contact with water, the investigated lacquers have different behaviour. The alkyd-epoxy-melamine lacquer (L-528) in the first approximately 300 h of immersion in water has a relatively high absorption rate of about 5 x 10^{-3} % / h, after which the water absorption rate decreases to about 0.65 x 10^{-3} % / h, and after 720 h of immersion the water absorption rate was 1.76 %.

In both epoxy and polyurethane lacquers, a period of initiation (up to about 200 h) is observed, followed by a period with relatively high absorption (200 - 400 h) after which the water absorption is limited asymptotically. After 620 h of exposure, the epoxy lacquer absorbs 1.4 % water while the polyurethane based lacquer - 0.93 % absorbs.

The dielectric loss evolution during immersion in water of the alkyd-epoxy-melamine lacquer is shown in Figure 2.

From Figure 2 it is observed that at frequencies below 1500Hz (industrial frequency range and its harmonics), the reference lacquer alkyd-epoxy-melamine (L-528) (without storage in water) has a
frequency dependent dielectric loss, with an average value of about $tg\delta = 0.013$. As a result of immersion in water, $tg\delta$ increases in time, reaching an average value of about 0.02 after 624 h of immersion (increase of about 2 times). At frequencies higher than 1500 Hz the $tg\delta$ frequency dependence is less pronounced having an average of about $tg\delta = 0.011$ for the reference sample, reaching 0.014 after 624 h of immersion (an increase of about 27 %).

The evolution of dielectric loss during water immersion for the polyurethane-based lacquer is shown in Figure 3.

![Figure 3. The dielectric loss evolution of the L-S lacquer as a result of water absorption](image)

Analysing Figure 3 it is found that the lacquer based on polyurethane (L-S) shows a similar frequency evolution after the immersion in water, too. The difference is that, after immersion in water (for 624 hours), the increase of $tg\delta$ is much less pronounced.

At frequencies lower than about 1700 Hz, the value of $tg\delta$ increases from an average value of 0.0069 (reference value) to about 0.0098 (about 42 %) while at higher frequencies, the value of $tg\delta$ increases from about 0.0058 to 0.0072 (about 24 %).

The dielectric loss evolution during immersion in water for the epoxy lacquer is shown in Figure 4.

![Figure 4. The dielectric loss evolution of L-G lacquer as a result of water absorption](image)

The dielectric behaviour of the epoxy (L-G) lacquer is different from that of the alkyd-epoxy-melamine and polyurethane lacquers. Thus, in Figure 4 are shown three distinct frequency domains respectively below 4kHz, for which $tg\delta$ is strongly frequency dependent (increases with decreasing of frequency), between 4 and 8 kHz the frequency influence on $tg\delta$ is insignificant, and at frequencies higher than 8kHz, $tg\delta$ shows a decreasing trend with the frequency increasing.
It is found that in all three frequency domains, \( \text{tg}\delta \) increases during the immersion in water. Thus, after 624 h of immersion the dielectric loss increases, with about 11%. Analysing the data in Figures 2 - 4 and comparing them, it is found that systematically, for both reference and immersed samples in water, the lowest values of \( \text{tg}\delta \) were recorded for the polyurethane (LS) based lacquer followed by the values for the epoxy lacquer (LG), while the alkyd-epoxy-melamine lacquer has the highest values (L-528). This hierarchy coincides with the values reported in [9, 20] for these lacquers.

The results of the volumetric resistivity determinations measured in DC indicated average reference values of 80.1 x 10\(^{15}\) \( \Omega \) cm for the polyurethane (LS) based lacquer, 66 x 10\(^{15}\) \( \Omega \) cm for the epoxy (LG) lacquer, respectively 20.2 x 10\(^{15}\) \( \Omega \) cm for the alkyd-epoxy-melamine (L-528) lacquer. These values are in good agreement with those reported in [9].

These values decrease systematically with the increase of the immersion times of the lacquer samples in water. Thus, after 720 h of immersion, the volumetric resistivity reaches values of 78.9 x 10\(^{15}\) \( \Omega \) cm for LS (decrease of about 13.7 %), to 64.5 x 10\(^{15}\) \( \Omega \) cm for LG (decrease of about 22.7 %) respectively to 15.2 x10\(^{15}\) \( \Omega \) cm for L-528 (decrease of about 24.8 %). It is found that is a good correlation between the increases of \( \text{tg}\delta \) and the volumetric resistivities decreases of the investigated lacquers due to water uptake.

The TG, DTA and DTG thermograms recorded on the initial alkyd-epoxy-melamine lacquer (reference) and after 720 h immersion in water are shown in Figure 5, respectively Figure 6.

![Figure 5. Initial thermograms (reference) recorded on sample L-528 lacquer](image-url)

Analysing Figure 5 it is found that after 140 °C a continuous mass loss (TG curve) up to about 650 °C occurs and the total mass loss is 95.5 %.

Analysing the DTA curves in correlation with DTG curves, two endothermic processes (phase transformation) stand out, one at 207.5 °C (less pronounced) and the other one at 367.0 °C. At higher temperatures (\( T_{\text{max1}} = 406.3 \) °C, \( T_{\text{max2}} = 450.2 \) °C and \( T_{\text{max3}} = 559.4 \) °C), three exothermic oxidation processes can be seen.

By comparative analysis of Figures 5 and 6 it is observed that after the alkyd-epoxy-melamine lacquer immersed in water for 720 h, there are no changes on the TG curve which indicate that the water absorbed during the immersion completely disappears during the drying of the samples analysed at room temperature.
Changes are observed on the DTA and DTG curves, respectively, where in the case of the immersed lacquer it stands out a single endothermic process of phase transformation at 373.1 °C and an increase of the maximum temperatures of the second exothermic oxidation process takes place, at 453.7 °C, the rest of parameters remaining within the limits of the experimental errors. These aspects lead to the conclusion that L-528 lacquer can be used in electrical applications only up to 140 °C (when the mass loss process begins).

The changes found on the DTA and DTG curves suggest that during the immersion, between water and L-528 lacquer, chemical processes (probably by addition to double bonds) take place modifying the polymer structure. The thermograms TG, DTA and DTG recorded on the initial epoxy (L-G) lacquer (reference) and after immersion in water for 792 h are shown in Figure 7, respectively Figure 8.

Analyzing Fig. 7 it is observed that at progressive heating of the epoxy (L-G) lacquer a continuous mass loss (TG curve) between 150 and 800 °C when a total mass loss of $\Delta m$ of 97.79 % is reached. On the DTA curves correlated with DTG curves, three endothermic processes (minimum DTA) stand out, which indicates that LG lacquer has a heterogeneous structure, respectively it contains three distinct phases with different melting points of $T_{m1} = 321.8 ^\circ C$, $T_{m2} = 390 ^\circ C$ and $T_{m3} = 403.4 ^\circ C$. These phases decompose simultaneously through a single major exothermic process of thermooxidation which is seen at maximum speed at $T_{max} = 597.5 ^\circ C$. 

Figure 6. Thermograms recorded on sample L-528 lacquer after 720 h of immersion in water

Figure 7. Initial thermograms (reference) recorded on sample L-G lacquer

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Comparing Figures 7 with figure 8, no changes on the TG curves are observed at temperatures below 150 °C, indicating that the water absorbed during immersion is completely eliminated during air drying at room temperature. On the other hand, it is observed that during immersion in water the material was homogenized, respectively, a single endothermic process is distinguished (a single phase with melting temperature $T_{m1} = 428.8 \, ^{\circ}C$). There is also an increase in mass loss in the range 300 - 450 °C, reaching $\Delta m = 80.59 \, %$ at 500 °C compared to 60.86 % in the case of the reference sample. These aspects lead to the conclusion that the L-528 lacquer can be used in electrical applications, only up to 160 °C (when the mass loss process begins).

The thermograms TG, DTA and DTG recorded on the lacquer based on polyurethane (L-S) (reference) and after 792 hours immersion in water are shown in Figure 9, respectively Figure 10.

From Figure 9 a continuous mass loss (TG-curves) of the lacquer based on polyurethane (L-S) starting at 280 °C and ending at around 600 °C when a total mass loss of $\Delta m_t$ of 96.54 % is reached, can be observed. This aspect suggests that L-S lacquer can be used in electrical applications up to 280 °C (double from than L-528 and L-G lacquers).
From the DTA and DTG diagrams, an endothermic process with a minimum pronounced DTA is identified, indicating a high crystallinity (degree of structural ordering) of the polymer, the melting process taking place at a temperature of $T_m = 374.4\, ^\circ C$.

After melting the material, the thermal decomposition is performed through several successive thermooxidation exothermic processes.

![Figure 10. Thermograms recorded on sample L-S lacquer after 792 h immersion in water](image-url)

A comparative analysis between Figures 9 and 10 showed that the two TG curves do not present significant differences. There is no increase in mass loss at temperatures below 300°C on the immersed water sample, indicating that the water absorbed during immersion is completely desorbed by drying in air at ambient temperature.

Analizing the DTA curves it is found that after immersion in water for 792 h the melting temperature drops from 383.5 to 373.4°C, suggesting that during the immersion, between water and polymer, chemical processes take place leading to the polyurethane structure changes.

The comparative analysis of the experimental results obtained shows the superiority in electrical applications of the L-S lacquer which does not present mass losses (structural changes) up to 280°C (two times higher than L-528 and L-G lacquers). The L-S lacquer has a volume resistivity with about 21% higher than L-G lacquer and with about 300% than L-528 lacquer, and has substantially lower water uptake and dielectric loss than L-528 and L-G lacquers.

4. Conclusions

Through determinations of gravimetric, volume resistivity, dielectric spectroscopy and a comparative thermal analysis (TG, DTA and DTG), interactions between distilled water and three different types of alkyd-epoxy-melamine, epoxy and polyurethane lacquers were studied. From the experimental determinations it resulted that:

- after 700 immersion hours of the samples analyzed in water at ambient temperature, the alkyd-epoxy-melamine based lacquer has a maximum water uptake of 1.76%, followed by the epoxy lacquer 1.4% and the polyurethane lacquer 0.93%;
- by thermal analysis it was found that the water retained by the investigated polymers does not change the TG diagrams in the temperature range up to 150°C, suggesting that the weight gain of the samples during immersion is due to chemical processes between water and polymer (probably-addition to double bonds) by which the chemical structure of the polymer changes. This aspect is also supported by the changes recorded in the DTA and DTG diagrams;
after immersion in water of the investigated lacquers, there was an increase of dielectric loss and a decrease of the volume resistivity (measured in DC), process that is probably due to the polar groups (–OH) increase in the polymer structure, at the contact with water. By comparative analysis of the experimental data obtained it was concluded that, in electrical applications, the lacquer L-S (polyurethane) is more indicated comparative to the lacquers L-528 (alkyd-epoxy-melamine) and LG (epoxy) because it has no mass loss (structural changes) up to at 280°C and it has a higher volume resistivity.

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