



RHEOLOGICAL BEHAVIOUR OF SOME DISPERSIONS FOR LONG LASTING PROTECTION OF COPPER-ALUMINIUM CONTACTS IN POWER TRANSMISSION EQUIPMENT

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Electric and heat conducting coatings with good heat and corrosion resistance for long lasting protection of copper-aluminium electric joints on degradation in power transmission equipment were obtained using a low viscosity epoxy resin as heat resistant binder, non-leaving aluminium powder paste and graphite as heat and electric conducting pigments, titanium dioxide and red iron oxide as anticorrosive pigments, a solution of a low molecular weight unsaturated polycarboxylic acid polymer as wetting additive, a polysiloxane copolymer as dispersing additive and n-butyl acetate as carrier. In view of establishing of optimum amount, three amounts of rheologic modifier based on a solution of a modified urea (BYK E410) was introduced into the selected base dispersion to make it more viscous at rest and thixotropic – more fluid under shear stress. Stationary rheological measurements show that the dispersion containing 40% epoxy resin, 20% aluminium pigment and 1% rheologic modifier BYK E 410 is the optimum one from the point of view of application, while the dynamic rheological behaviour shows that it has the highest elasticity.

INTRODUCTION

The interface of copper-aluminium electrical connections – the two most commonly used materials as conductors in electrical equipment – deteriorates in time, which produces energy losses and/or outcomes of energetic installations or equipment. The most put in danger are those connections making the joint between the transformer plants and/or electric branch and open-air or underground joining power lines. That is why a preventive maintenance of effective electrical connections for power circuits must be assured.

The main electric stresses to which the copper-aluminium electrical connections are subjected are the thermal and chemical ones. The first are due to the energy losses by the Joule-Lenz effect, eddy flow, hysteresis losses or losses in the dielectrics placed into the electrical fields and the second one to corrosion.

The deterioration of joints depends on the type of contact performed during their assembling and consists of protruding of humidity and pollutants – having as result the overheating and/or electrochemical corrosion of aluminium, forming on surface of corrosion products of copper – producing heating and/or fault of contacts, exfoliation of zinc coated clamping jaws under the action of working thermal conditions due to the difference between the expansion coefficients of the two metals. So the nature of the processes producing into the contact zone is very different, all are related with the degradation of the contact surfaces.

To prevent their degradation, the copper-aluminium electric joints are protected usually by plating with silver or tin, but surprising degradation phenomena under the action of environmental conditions were found for such protections. An alternative can be the protection with organic coatings.¹⁻³ But such coatings must

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conduct heat and electricity and have high anticorrosion capacity and heat resistance. Recently, aluminium powder was used as fillers for epoxy adhesives improving the electrical and thermal conductivity as well as mechanical properties.⁴⁻⁶

The objective of the present paper is the preparation of some solvent-based coatings designed for long lasting protection of copper-aluminium electric joints on degradation and their stationary and dynamic rheological characterization in view of selecting the most performing from application view point.

RESULTS

The rheograms obtained for dispersions having the same composition but different resins as binder are shown in Fig. 1.

The hysteresis loops for dispersions having as binder epoxy or silicon resin are presented in Fig. 2.

The rheograms of dispersions with binder/aluminium pigment ratio 2/1 and 1/1 are given in Fig. 3.

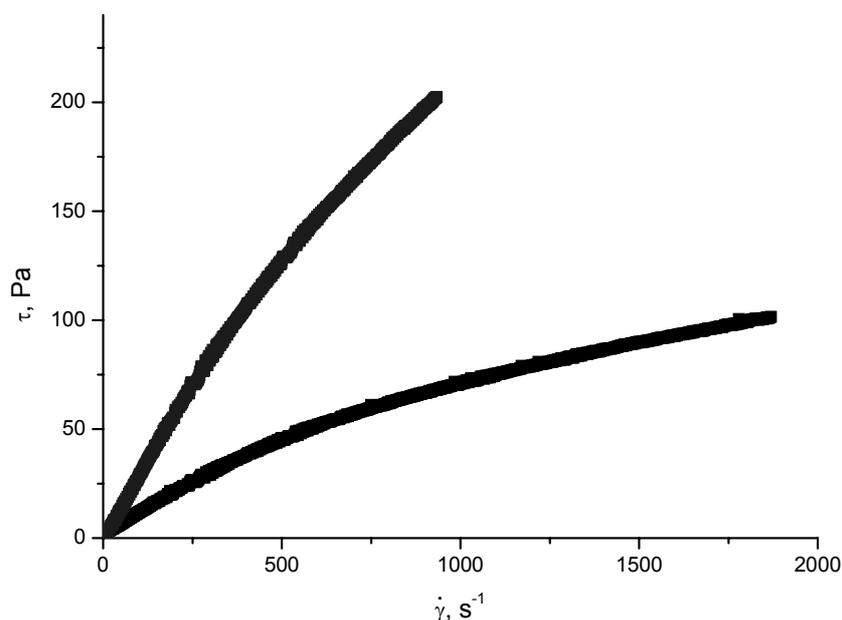


Fig. 1 – Rheograms of dispersions having as binder: epoxy resin – lower; silicon resin – upper and the same composition.

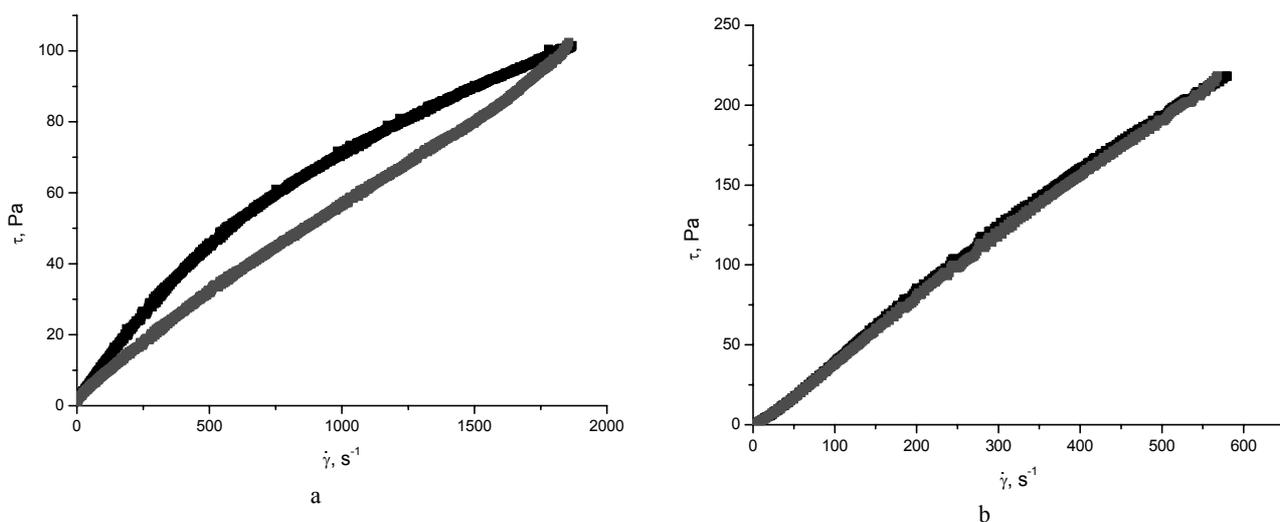


Fig. 2 – Hysteresis loops for dispersions having as binder: a – epoxy and b – silicon resin; upper curves – increasing and lower – decreasing of shear rate.

Per cent compositions of the reference and of dispersion containing the specified amounts of rheological modifier BYC E 410 is presented in Table 1.

The rheograms of formulations from Table 1 are shown in Fig. 4, with a detail at low shear rates.

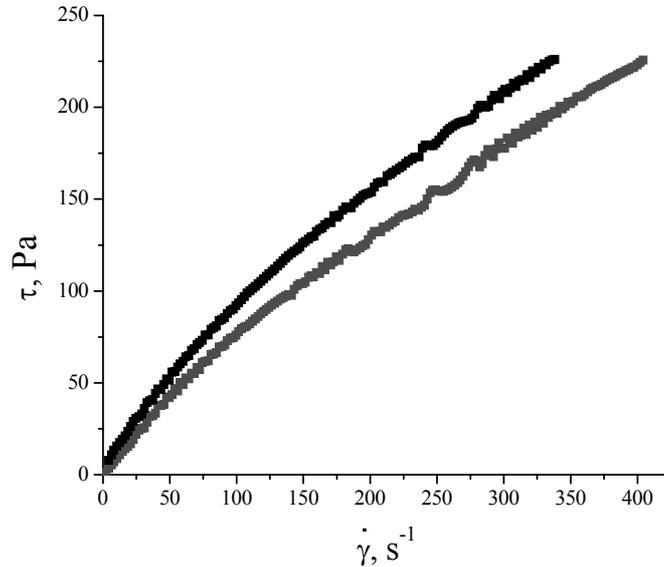


Fig. 3 – Rheograms of dispersions having binder/aluminium pigment ratio: 2/1 – upper; 1/1 – lower.

Table 1

Percent weight composition of reference and dispersion containing different amounts of rheologic additive BYK E 410

Component / % in dispersion	Reference (1)	Dispersion 2	Dispersion 3	Dispersion 4
Epoxy resin	40.36	40.12	39.88	39.66
Wetting and dispersing agents	0.60	0.60	0.60	0.59
Anticorrosive agents:				
TiO ₂	15.13	15.05	14.96	14.87
Fe ₂ O ₃	5.04	5.02	4.99	4.96
Graphite	3.02	3.01	2.99	2.97
Aluminium paste	20.18	20.06	19.94	19.83
Rheologic additive BYC E 410	0	0.50	1.00	1.47
n-Butyl acetate	15.64	15.64	15.64	15.64

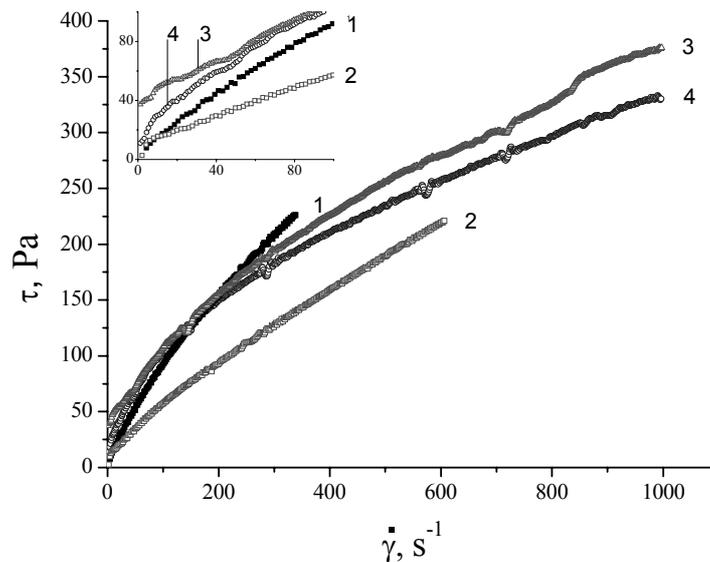


Fig. 4 – Rheograms obtained for dispersions from Table 1.

The rheological parameters obtained for the dispersion from Table 1 using the equation Ostwald-de Waele (the first two) and Herschel–Bulkley (the last two) are given in Table 2.

The hysteresis loops for dispersions 3 and 4 are presented in Fig. 5a,b.

The results of the dynamic measurements for dispersions from Table 1 are presented in Fig. 6.

Table 2

Rheological parameters obtained for dispersions from Table 1

Sample	τ_0 , Pa	η_0 , Pa.s	n	r^2
1 Reference	0	2.99	0.744	0.99949
2	0	1.69	0.759	0.99933
3	21.2	26.39	0.611	0.99821
4	12.3	10.00	0.508	0.99807

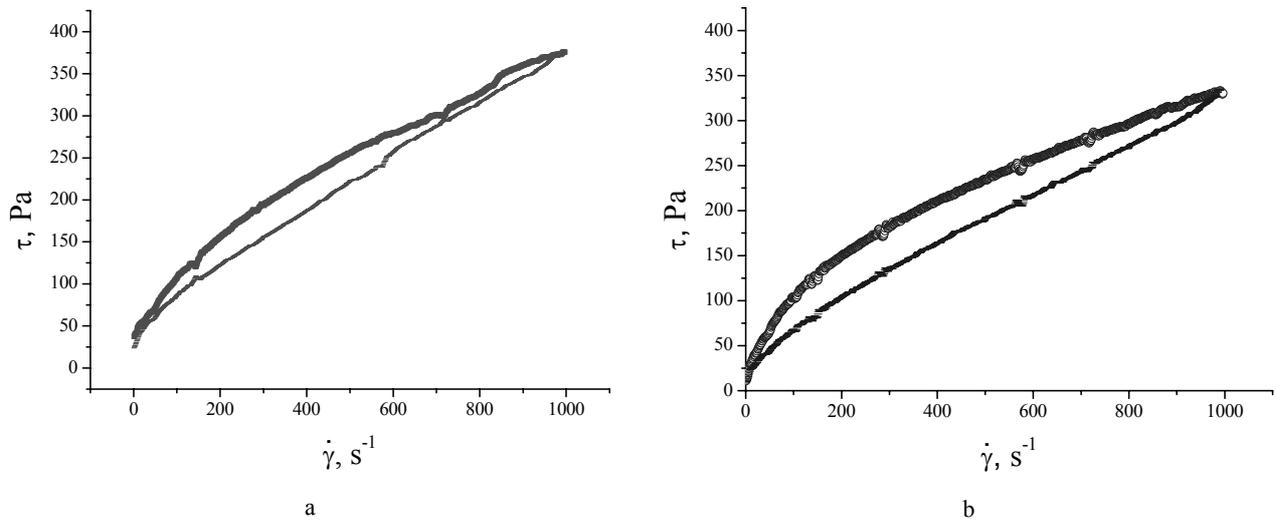


Fig. 5 – Hysteresis loops for dispersions: a – 3; b – 4.

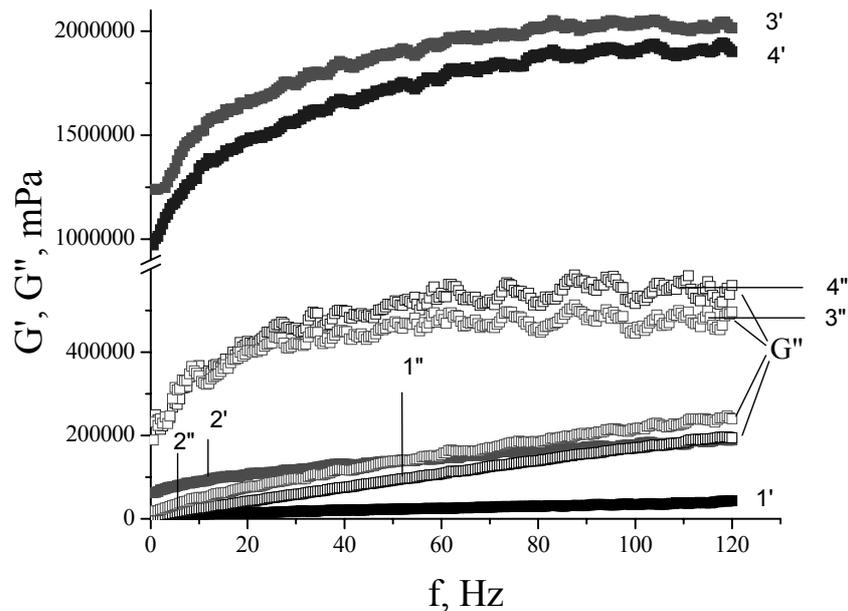


Fig. 6 – Dependence of storage (G') and loss (G'') moduli on frequency: 1,1' – reference; 2',2'' – 0.50%; 3',3'' – 1.00% and 4',4'' – 1.47% rheologic modifier.

DISCUSSION

Organic coatings are extensively studied due to their wide range of applications.^{1,2}

A formulation of a heat and electric conductive, heat resistant and highly anticorrosive coating must contain, as any other coating, binder, pigment(s), additives, and carrier. It is said that the first two components perform the corrosion protection work in the cured paint.³ If it must be heat and electric conductive it has to provide these properties. The other components contribute also to the coating quality.

The binder, usually an organic polymer, binds to pigments and additives and to the metal surface, providing the physical structure which supports and contains the components.¹ The amount of oxygen, ions, water or UV radiation penetrating into a cured coating layer depend to some extent on the polymer used, because a very thin layer of polymer forms on the surface. This layer ensures also the heat resistance.

Pigments provide corrosion protection, colour, and – if they are metallic – heat and electric conductivity, functioning also as fillers. Anticorrosion pigments act in the cured coatings, in barrier ones must be inert, while filler pigments must be inert all the time.

Additives may modify some coating's properties: improve processing, compatibility of the raw materials, application and cure or add new functional application.^{3,7} One of the most important additives for the protection of metals from corrosion is metallic particles, as aluminium ones.⁸⁻¹⁵ The good conductivity of the pigment is used in electric and magnetic shielding, discharge of static electricity in plastics, radar inhibitors, etc.

The carrier is the vehicle that carries all the other components in the uncured paint. It can be an organic solvent or water. Solvent-based paints present some advantages compared with water-based ones: in water-based paints the pH is higher than 8-9, so it is necessary to add corrosion inhibitors, generally environmental hazardous, to avoid metallic pigments corrosion.^{10, 16-20} Moreover, when water is present, the metal particles – such as those of aluminium – can be oxidized.

Metals can be added both as spherical or flakes particles, which have a higher surface area to weight ratio than spherical ones and a greater contact area.²¹ Metallic pigments are used as pastes, often coated with a polymer film to guarantee good adhesion to the organic binder,²² which also affects the material properties.

Coatings with pre-established properties are obtained by a careful selection of the above mentioned components. To obtain heat and electric conducting coatings with good heat and corrosion resistance for long lasting protection of copper-aluminium electric joints on degradation a low viscosity epoxy resin and a silicon one were selected as heat resistant binders, non-leaving aluminium powder paste and graphite as heat and electric conducting pigments, titanium dioxide and red iron oxide as anticorrosive pigments, a solution of a low molecular weight unsaturated polycarboxylic acid polymer as wetting additive, a polysiloxane copolymer as dispersing additive, and n-butyl acetate as carrier. A solution of a modified urea (BYK-E 410) was used as rheologic modifier. All the additives are recommended by BYK Additives & Instruments for such dispersion. Aluminium is a non-toxic material,²³ complying well with the current environmental protection standards.²⁴

The knowledge of the rheological properties of coating formulations are very important for their application on substrate, behaviour at the application site, processing, handling, the process design and the product development.²⁵ Stationary method gives information on the type of flowing, dynamic viscosity, capacity of flowing, consistency, spreadability and dependence of rheological behaviour on time. The dynamic one allows the establishing of contribution of elasticity and viscosity to their viscoelastic behaviour of dispersions. They are influenced by the type of binder, nature, size and form of pigments – both metallic and anticorrosion, additive used (especially rheologic) and nature of carrier.

Selection of binder. The coatings' heat resistance can be monitored by choosing proper binders. Some epoxy and silicon resins are recognized as heat resistant and metal adherent.

The rheograms of disperse systems containing the same amount of components, given in Fig. 1, show that the viscosity of the dispersion containing epoxy resin as binder presents a dramatic shear thinning with increasing shear rates, that is the dispersion is highly pseudoplastic, while the one based on silicon resin is less sensitive to shear. The values of dynamic viscosities emphasize that when epoxy resin is used the dynamic viscosity have higher value when $\dot{\gamma}$ is increased (0.85 Pa.s) and much lower when it is decreased (0.15 Pa.s). This signify that using of epoxy resin results in higher dynamic viscosity and thixotropy. Silicon resin

gives lower viscosity for increasing (0.58 Pa.s) and higher for decreasing (0.47 Pa.s) shear rates. Consequently, from application point of view the epoxy resin is the most convenient binder, it giving dispersion with high viscosity at rest and low when a force is applied.

The hysteresis loops of the two dispersions containing aluminium particles having the same shape – non-leafing – are given in Fig. 2a, b. It shows that the epoxy resin-based dispersion displays a prominent hysteresis loop, while that containing silicon resin an almost imperceptible one. This means that the last dispersion, practically non-thixotropic, will be applied more difficultly. The results also suggest that the epoxy resin is a better binder.

Selection of binder and aluminium pigment concentrations. To establish the most convenient binder and metal pigment concentrations, two dispersions having the same sum of percentages of binder and pigment – 40% binder and 20% pigment, 30% binder and 30% pigment respectively – and constant amounts from the other components were prepared. Fig. 3 shows that the rheogram of the dispersions containing more binder is placed above the one containing higher amount of aluminium paste. The dynamic viscosity of the first dispersion is 2.99 Pa.s, while of the second one 1.96 Pa.s. This demonstrates that the main contribution to viscosity is brought about by the resin. So, the composition containing more resin was selected to establish the influence of the rheologic modifier on coating rheological behaviour.

Selection of concentration of rheologic modifier. To select the proper amount of rheologic modifier, the dispersions from Table 1 were prepared, having practically the same composition, excepting the rheologic modifier, which varies between 0.50 and 1.47%. Their rheograms, presented in Fig. 4 with a detail at low shear rates, reveal that at low shear rates, ranging between 0 and about 20 s⁻¹, their position displace upward with increasing of rheologic modifier concentration as expected. If this value is surpassed the formulation containing the minimum amount of rheologic modifier (2) becomes more sensitive to shear rates, while the other two continue to be placed above the reference. This happens until the shear rate reaches about 80 s⁻¹, value after which the rheograms of dispersion 3 and 4 superpose until about 200 s⁻¹. Then the rheogram for dispersion 3 is placed above that of 4; also, starting with 200 s⁻¹ the reference rheogram has the highest position. This can be explained if the mode of action of rheologic additive into the dispersion is

considered: it builds a three-dimensional structure, which makes the dispersion more viscous and thixotropic. This three-dimensional structure destroys under the action of higher shear stresses.

The reference and dispersion containing the minimum amount of rheologic modifier start to flow at a shear stress very close to zero, while the others two present limiting shear stress. To determine their rheological parameters the rheograms of the first two dispersions were fitted with Ostwald-de Waele equation:²⁶

$$\tau = K \dot{\gamma}^n \quad (1)$$

and the last two with Herschel–Bulkley one:²⁷

$$\tau = \tau_0 + K \dot{\gamma}^n \quad (2)$$

where τ is the shear stress, $\dot{\gamma}$ – shear rate, τ_0 – limiting shear stress, K and n – consistency and flowing indices respectively.

The obtained values, given in Table 2, show that, surprisingly, the highest dynamic viscosity and limiting shear stress is presented by the dispersion 3, which contains 1.0 % rheologic modifier. But it has higher flowing index than dispersion 4, which means that however the last dispersion has the lowest fluidity.

The rheograms obtained with increasing and decreasing shear rates superpose for dispersion 2, which signifies that it is non-thixotropic. On the other hand dispersions 3 and 4 present pretty large hysteresis loops, as can be seen in Fig. 5a, b.

The area of the loop indicates the energy required to breaking down the thixotropic structure²⁸ and it is a measure of thixotropy. It is useful for demonstrating the thixotropic behaviour, but is only a qualitative measure of thixotropy, depending on the parameters defining the hysteresis loop: maximum shear rate as well as the length of time of increasing/decreasing shear rates.^{29,30} A quantitative measure of thixotropy is the relative hysteresis area, called also thixotropic index, defined as the ratio of the area of hysteresis loop to the area beneath the ascending shear curve.²⁹

The surface of hysteresis loop of dispersion 4 is higher than of dispersion 3, which is reflected in the values of the thixotropic indices, they having the values 0.10 and 0.16 respectively. This means that the shear forces disorganize strongly the three-dimensional structure of the dispersion containing the maximum amount of additive, by temporary disruption of physical bonds by the shear force, and alters the viscosity.³¹ But both dispersions

remake completely their structure, the rheograms superposing at low shear rates. Consequently, the most convenient is dispersion 3, preventing better the settling and improving anti-sagging.

The dynamic rheologic behaviour of dispersion from Table 2 is shown in Fig. 6. Unlike the stationary experiments which destroy the internal organization and structure of dispersion, the oscillatory measurements change their rheology in only a very minor way as a result of the experiment.

The Fig. shows that the reference is preponderantly viscous over the whole frequency range (loss modulus, G'' , is higher than the storage one, G') and viscosity increases a bit with frequency. If 0.5% rheologic modifier is added the dispersion becomes slight elastic at low frequencies, a crossover point appears at about 50 Hz, after which the viscosity prevails; dispersion becomes less fluid with frequency increase. Dispersion 3 and 4, containing 1.0 and 1.47% respectively, are prevalently elastic over the whole frequency range, but the highest elastic character is displayed by dispersion 3. The viscosities of the two dispersions are roughly the same at low frequencies, up to about 10 Hz, than the last dispersion becomes more viscous, especially when the frequency is higher than about 25 Hz; after about 50 Hz the viscosities become independent on frequency. This suggests that dispersion 3 has the optimum composition, presenting the highest dynamic viscosity, limiting shear stress and elasticity but being less viscous during application.

EXPERIMENTAL

Preparation of dispersions. Dispersions were prepared in a Dispermat CN10 dissolver (VMA-GETZMANN GmbH Germany) using as binder a low viscosity epoxy resin having the epoxy equivalent weight 180-220 g and a viscosity at 25°C of 500-900 mPa.s (LEUNA-Herze GmbH, Germany) or a phenyl methyl siliconic one (Bayer Silicones, Belgium, viscosity at 23°C 791 mPa.s, non-volatile content at 125°C and 60 min – 77.1 %), a solution of a low molecular weight unsaturated polycarboxylic acid polymer and a polysiloxane copolymer (BYK-Chemie GmbH, Germany) as wetting and dispersing additives respectively, titanium dioxide (Delta Chemicals, residue on sieve of 45 μm less than 0,01%) and red iron oxide (Chimica Orăștie, residue on sieve of 63 μm less than 0,3%) as anticorrosive pigments, non-leafing aluminium powder paste (Schlenk Metallpulver GmbH&Co.KG Germany, average diameter 14 μm , residue on 45 μm sieve – maximum 0.3%, concentration 64.5%) and graphite (Merk, Germany, carbon 88-98%, residue on 0.16 mm sieve – 10-15%) as heat and electric conducting pigments and n-butyl acetate (Chimopar) as solvent. The order of introducing of components into the resin under stirring was: wetting and dispersing additives, titanium dioxide and red iron

oxide (800-1000 rpm), aluminium paste (300-400 rpm), graphite and n-butyl acetate. In some dispersions BYK E 410 (BYK-Chemie GmbH, Germany), a solution of a modified urea, was used to modify the rheological properties.

Stationary rheological behaviour was determined at $25 \pm 0.1^\circ\text{C}$ using a rotational viscometer Hake VT 550 equipped with the MV1 sensor system for medium viscosity and RheoWin 4 Thermo Fischer Scientific software.

Dynamic (oscillatory) rheological measurements were made at room temperature (23°C) with a Micro Fourier Transform Rheometer MRF 2100, GBC-Australia, under squeezing flow using the following parameters: frequency range 0-140 s^{-1} , 280 discrete frequencies simultaneously analyzed in range by a step of 0.5 s^{-1} , 30 spectra consequently acquired every tested sample, gap between the upper and bottom plates – 400 μm , displacement amplitude – 0.03 μm to fall into the linear viscoelastic domain. The very small amplitude of the pseudorandom squeezing motion exerted on the viscoelastic sample allows the continuous monitoring of the force transmitted through it to the force sensor (bottom plate). The displacement and force lead, by a Fourier transform processing, to the storage and loss modulus at every individual frequency step within the employed frequency range.

CONCLUSIONS

Heat and electric conducting coatings with good heat and corrosion resistance for protection of copper-aluminium electric joints on degradation were designed using a low viscosity epoxy resin as heat resistant binders, non-leafing aluminium powder paste and graphite as heat and electric conducting pigments, titanium dioxide and red iron oxide as anticorrosive pigments, a solution of a low molecular weight unsaturated polycarboxylic acid polymer as wetting additive, a polysiloxane copolymer as dispersing additive and n-butyl acetate as carrier.

Stationary rheological properties show that the dynamic viscosity of dispersion containing 40% binder and 20% aluminium pigment is 1.52 times higher than of that containing 30% from both components, which made the first formulation to be selected for establishing the influence of concentration of rheologic modifier on dispersion behaviour.

Dispersions become thixotropic if 1.00 and 1.47 % rheologic modifier is introduced. The most convenient from the point of view of application is the first dispersion, being more viscous at rest and thus preventing better the settling and improving anti-sagging.

Dynamic rheologic behaviour shows that the highest elastic character is possessed by the dispersion containing 1.00% rheologic additive, a bit less viscous than that containing 1.47%, especially at frequencies higher than about 25 Hz. This suggests that this dispersion has the optimum

composition, presenting the highest dynamic viscosity, limiting shear stress and elasticity but being less viscous during application.

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