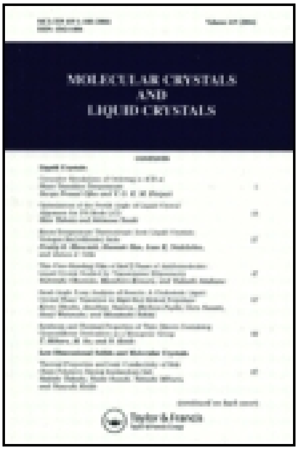

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Oils Polymerization Induced by Corona Discharges at Atmospheric Pressure

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OILS POLYMERIZATION INDUCED BY CORONA DISCHARGES AT ATMOSPHERIC PRESSURE

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High reaction rate mechanisms of oils polymerization are reported in a wire-to-plane corona discharge electrode configuration at atmospheric pressure. Spectral measurements are performed at different stages of the polymerization process, as well as optical investigation of the oil polymer layers.

INTRODUCTION

Corona discharges are widely applied in surface materials treatments due to the generation of free radicals, which improve the material surface properties by inducing chemical reactions.

In this paper we investigate by infrared (IR) spectral measurements the mechanisms with a high reaction rate associated to oils polymerization induced in a wire-to-plane corona discharge electrode configuration at atmospheric pressure. Also, we analyzed by optical microscopy the obtained polymer layers, which could be used as protecting layers for metallic surfaces against the environment factors.

EXPERIMENTAL SET-UP

The experimental set-up is schematically presented in Figure 1.

The corona discharge electrode configuration is of wire-to-plane type. The cathode E_1 is a thin copper wire of 40 mm length placed in air

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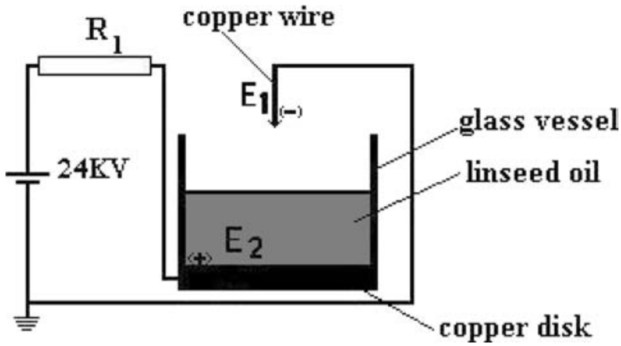

FIGURE 1 Scheme of experimental set-up.

at atmospheric pressure at 30 mm above the anode E_2, a copper disk with 80 mm diameter. The anode is situated in a linseed oil on the bottom of the glass vessel (80 mm diameter). The liquid thickness is of 10 mm. A high voltage of 24 kV is applied on the electrodes through a resistor of 100 MΩ.

In order to investigate the linseed oil polymerization mechanisms we performed IR spectral measurements. The linseed oil polymer film obtained under corona charge injection on a germanium substrate was also investigated spectrally by an IR 75 Specord spectrophotometer with a resolution of 5 cm^{-1}.

RESULTS AND DISCUSSIONS

In the corona discharge configuration presented above, at the free surface of the oil, which act as a virtual electrode [1], negative ions like O_2^-, O_3^-, O_4^-, CO_2^-, CO_3^- were generated [2]. These charge injections in the oil bulk induce free radicals, which initiate the polymerization radical chain reaction, a mechanism divided in three steps: initiation, propagation and termination.

In the first step the oil free radicals can be produced from the unsaturated fatty acids (like from the carboxylic functional group –COOH [3]). In the presence of the oxygen, the free radicals generated in this way in the linseed oil submitted to corona charge injection for 50 hours lead to peroxides radicals and consequently to hydro-peroxides and alcohols formation identified in IR spectrum in Figure 2 at 3400 cm^{-1} [4]. By comparison, the spectrum of the linseed oil kept in air is presented.

The hydro-peroxides are not stable, cleave in time and form free radicals ($ROO^{\cdot}$, $RO^{\cdot}$, OH). Both peroxyl ($ROO^{\cdot}$) and alkoxy ($RO^{\cdot}$) radicals formed in this process can attack a nearby double bond and the corresponding fatty

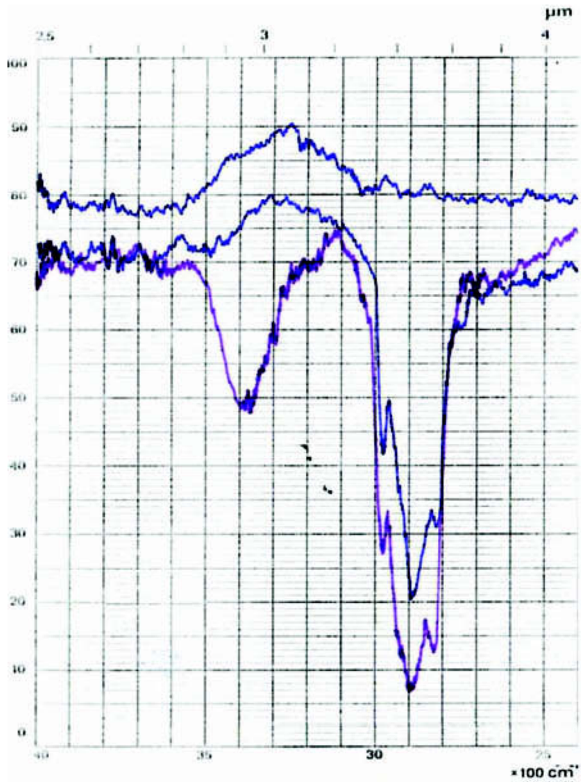

FIGURE 2 Detail from IR spectrum of linseed oil submited to corona charge injection for 50 hours (the dark blue spectrum) and of linseed oil kept in air (the blue spectrum).

acid is chemically linked to the fatty acid where the radical was present. This reaction consumes the attacked double bond as we can see in Figure 3 at 1650 cm^{-1}, but the free radicals are still available afterwards and can propagate the polymerization reaction [5]. In our case, the hydro-peroxides, the most important product in the second step of the polymerization mechanism, generate processes that lead in the linseed oil to the C–O–C polymer bonds identified in Figure 3 at 1060–1150 cm^{-1} [6]. The polymer C–O–C bond at 1060–1150 cm^{-1} is emphasized in IR spectrum of linseed oil polymer obtained after two hours of corona charge injection as it can be seen in Figure 4.

Linseed oil is the basic compound for paints, having protective surface properties against the environment factors [5]. The drying of the natural linseed oil takes time, the time being reduced only by adding chemical

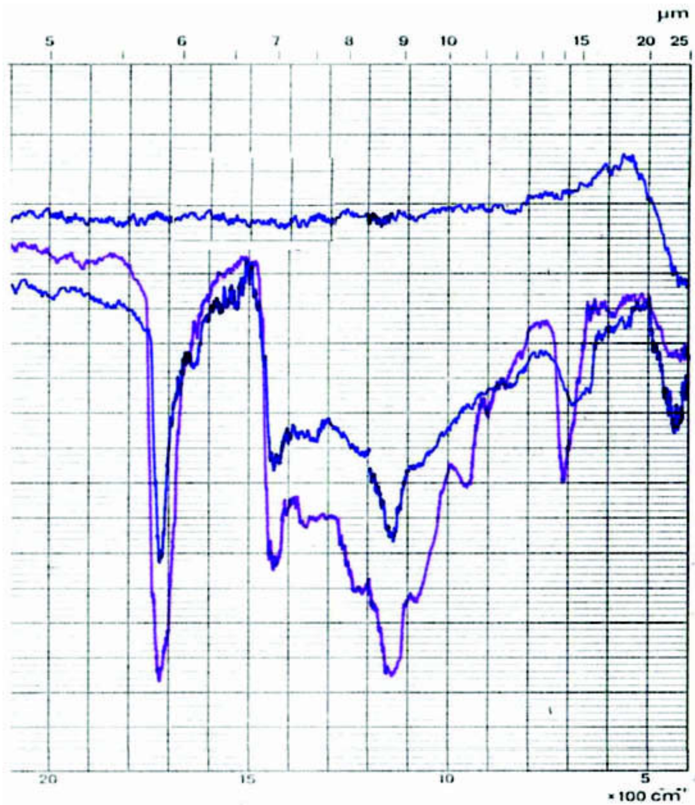

FIGURE 3 Detail from IR spectrum of linseed oil submited to corona charge injection for 50 hours (the dark blue spectrum) and of linseed oil kept in air (the blue spectrum).

compounds that accelerate this process. The use of these chemical compounds may be avoided by corona charge injection at the surface of the paint compounds.

In the Figure 5 it can be seen that a linseed oil polymer layer deposited on an unpolished substrate do not affect the substrate properties and follow the complex shape of the surface. This picture was obtained using a Carl Zeis microscope (with 500 times magnification) coupled to a video camera.

The convective movement of the dielectric liquid under corona charge injection [7] allows the uniform stretching of the liquid upon the metallic surface before the polymer formation. Therefore the polymer layers obtained afterwards in the corona discharge may coat complex geometrical and porous metallic surfaces.

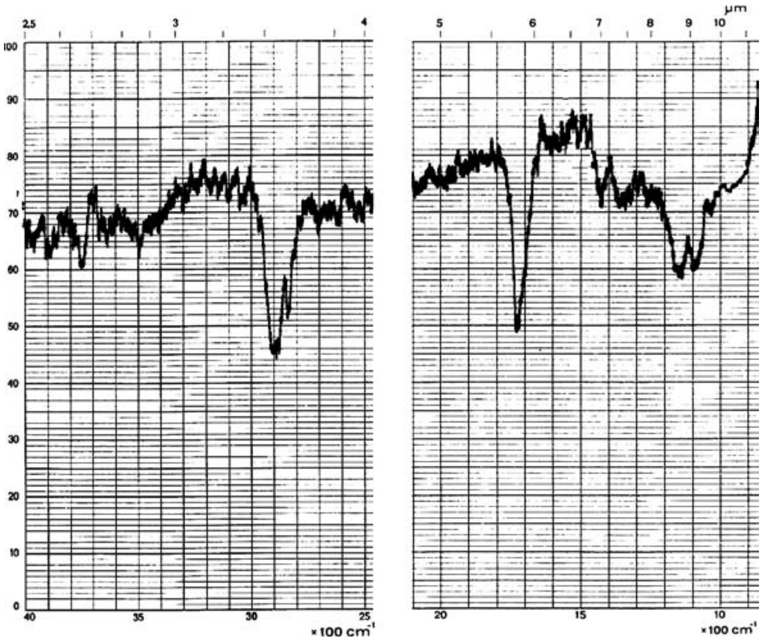

FIGURE 4 IR spectrum of linseed oil polymer layer obtained on a germanium suport after two hours of corona charge injection.

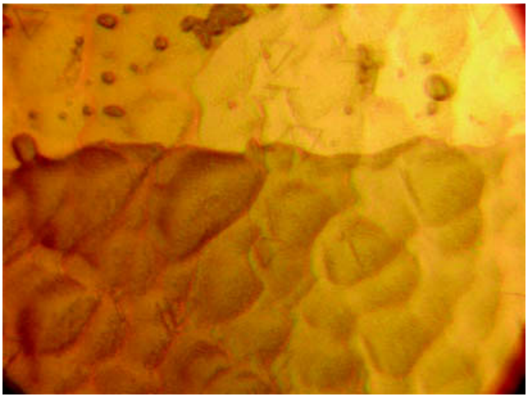

FIGURE 5 Linseed oil polymer layer deposited on a Si substrate.

CONCLUSIONS

Under corona charge injection the linseed oil is polymerized in two hours, comparing with ten days needed for air polymerization process. The high reaction rate polymerization mechanism is due to hydro-peroxide generation in liquid bulk by corona charge injection at the free surface of the oil, which acts as a virtual electrode. Due to liquid convective movement the entire metallic surface is coated with a uniform layer which can penetrates in all the surface pores. Corona discharges at atmospheric pressure polymerization allows the development of new polymer compounds starting from dielectric fluids precursors for archaeological objects protection.

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