

It has been established that the conductivity in lignin is intrinsic and belongs to the mixed type, the greatest contribution to it being made by the electronic and ionic components. An energy spectrum of the yield of photocarriers has been obtained.

The study of electrical conductivity and the type of carriers has become one of the common methods of elucidating the function and properties of biopolymers, especially lipids, carotenoids, carbohydrates, and chlorophyll [1].

The number of publications in which the electrical-conducting properties of lignin are considered is small. It has been established that the activation energy amounts to 36 kcal/mole, which is evidence in favor of an activation mechanism of conductivity [2]. There is a hypothesis that the conductivity of lignin is due to the presence of carbocations at phase-separation surfaces, but there are no substantiated proofs of this [3].

Since lignins are amorphous composition-inhomogeneous polymers differing considerably in functional composition according to the method of isolation, it may be assumed that the experimental conditions (temperature, water vapor pressure, presence of atmospheric gases) may lead to different conclusions concerning the type of carriers and the energy of their formation.

Our aim was to determine the energy yield of the carriers in the conductivity band from the action spectra of the photocurrent, and to determine the influence of the pressure of oxygen, of water vapor, and of hydrazine on the conductivity of lignin.

On the basis of the presence of functional groups (carboxy, carbonyl, quinoid, quinomethide, and phenolic units), the mixed type of conductivity in lignins may be assumed. In order to decide whether the electrical conductivity of lignin is intrinsic or due to impurities and to determine the spectral composition of the energy of generation carriers and their passage into the conductivity zone, we have compared the absorption spectrum of lignin with the action spectrum of a photocurrent.

The results, which are presented in Fig 1, show a satisfactory agreement of the absorption spectra and of the action spectra of the photocurrent, which indicates intrinsic, and not impurity, conductivity of this lignin preparation. Furthermore, the action spectrum of the photocurrent reflects the distribution of the intensity of the photocurrent as a function of the energy of a light quantum, since the energy of a quantum

$$\Delta E = \frac{282 \cdot 10^2}{\lambda} \text{ (kcal/mole),}$$

where  $\lambda$  is the wavelength of the incident light quantum.

The minimum work function of the carriers is determined from the "red limit" of the photocurrent. For the preparation of soda lignin studied, the "red limit" was in the range of 2.2-2.0 eV. This value of  $\Delta E$  agrees qualitatively with the "red limit" of the work function of free radicals on the irradiation of lignin (2.4-2.0 eV) [4].

It is known that an increase of conductivity in a semiconductor when an electron acceptor is present in the system leads to a rise in the whole conductivity, and the addition of electron-donating substances to the system leads to a rise in the electron conductivity. Thus, the use of additives possessing electron-accepting and electron-donating properties

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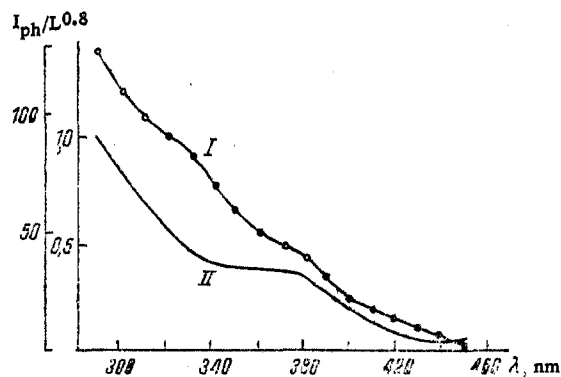


Fig. 1. Spectrum of the photocurrent (I) and absorption spectrum (II) of soda lignin.

will permit the type of conductivity or, in the case of the mixed type of conductivity, the contributions of the individual components to be determined [1].

As has been shown previously [5], for lignin an increase in conductivity (dark conductivity and photoconductivity) with a rise in the pressure of oxygen is characteristic, which is evidence in favor of a contribution of a hole component to the total electrical conductivity. A more considerable effect of an increase in conductivity (dark conductivity and photoconductivity) is observed on the admission of vapors of hydrazine ( $N_2H_4$ ) (Fig. 2). While the increase in current on the admission of oxygen is 2- to 3-fold, in the case of hydrazine the current increases tenfold. Consequently, the contribution of electron conductivity is greater than that of hole conductivity.

It must be pointed out that on the admission of hydrazine vapor the concentration of electron paramagnetic centers (EPCs) in the lignin decreased with time (Fig. 3), while oxygen had no such influence. The presence of moisture increases the conductivity of lignin at water vapor pressures of from  $140 \cdot 10^2$  to  $180 \cdot 10^2$  Pa (Fig. 2, curve II). The increase in the conductivity of lignin on contact with water vapor can be explained by the contribution of ionic conductivity due to the presence of ionogenic groups in the lignin on dissociation.

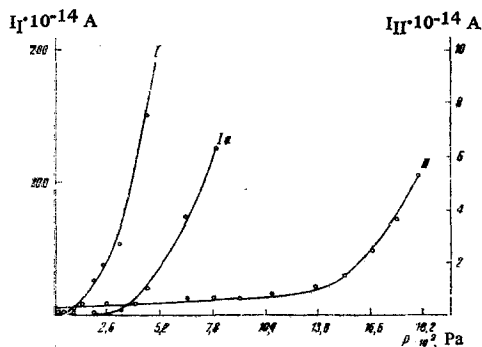


Fig. 2

Fig. 2. Influence of the pressure of water vapor on the dark current (II) and of the pressure of hydrazine vapor on the dark current (I) and on the photocurrent (Ia).

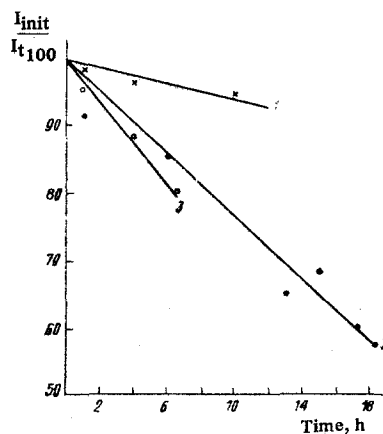


Fig. 3

Fig. 3. Change in the concentration of EPCs of soda lignin with time in hydrazine vapor for different samples.

Thus, lignins belong to dielectrics and semiconductors (depending on the conditions) with the mixed type of conductivity, their total conductivity being due to contributions from electron, hole, and ionic components.

On the basis of what has been said above, the results of the adsorption and grafting-on of lignin from solution onto lignin present in the solid wood residue in a soda cook is completely explicable qualitatively. The adsorption and secondary grafting-on of lignin from solution due to a difference between the lignins of the solid phase of the wood residue and those in solution with respect to their electron donor/acceptor properties [6] is determined by the striving for relaxation of the electrons of the surface (the electronic component of conductivity) with the components present in the solution, in which hole conductivity predominates. The levelling out of the difference in the lignins of the solid phase and those present in solution with respect to their redox properties and the change in the hole conductivity of the dissolved lignin into the electron type on the addition of additives possessing reducing properties lead to an inhibition of the secondary-grafting-on of lignin from the solution to the lignin present in the solid phase of the wood residue.

#### EXPERIMENTAL

The soda lignin was obtained from deresinified pinewood by a published method [7]. The absorption spectra of the soda lignin deposited from a dioxane solution in the form of a film on quartz glass were recorded on a SF-16 spectrophotometer. For investigating the dark conductivity and photoconductivity we used a vacuum apparatus [5] permitting the measurement of currents in the range of  $10^{-13}$ - $10^{-14}$  A. The source of light was a DKsÉL-1000 xenon lamp. In the investigation of the photocurrent we used electrodes of the scanning type prepared by sputtering silver on a fused quartz support. A film of the sample was deposited in the support from a solution of the lignin in dioxane.

#### SUMMARY

1. It has been established that lignins belong to the dielectrics and semiconductors (depending on the conditions of their preparation and of the experiment) with a mixed type of conductivity the total conductivity of which is due to the contributions of electron, ionic and hole components.

2. The work function of the current carriers in lignin in the conductivity zone is in the range of 2.2-2.0 eV.

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