

# FORMATION OF POLYMER DEPOSITS IN THE CORONA DISCHARGE OF BOTH POLARITIES IN CO AND ITS MIXTURES WITH H<sub>2</sub> AND H<sub>2</sub>O

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The formation of polymer deposits on the inner electrode of a coaxial system for the corona discharge was experimentally studied, when the corona discharge was burning in CO and mixtures of CO + H<sub>2</sub> and CO + H<sub>2</sub>O. The structural elements of deposits were determined by IR absorption spectrometry. On the applied Mo inner electrode formation of metal chelates was observed.

## ОБРАЗОВАНИЕ ПОЛИМЕРНЫХ СЛОЕВ В КОРОННОМ РАЗРЯДЕ ОБЕИХ ПОЛЯРИНОСТЕЙ, НАНЕСЕННЫХ В ОКИСЛЕ УГЛЕРОДА И ЕГО СМЕСЯХ С H<sub>2</sub> И H<sub>2</sub>O

В работе изучено образование полимерных слоев на внутреннем электроде коаксиальной системы в коронном разряде, происходящем в оксиде углерода и его смесях с H<sub>2</sub> и H<sub>2</sub>O. Структурные элементы нанесенных слоев были определены при помощи абсорбционной инфракрасной спектроскопии. На используемом молибденовом внутреннем электроде наблюдалось возникновение металлургических хелатных образований.

### 1. INTRODUCTION

The corona discharge belongs to the most frequently applied discharges in preparing thin polymer layers [1], besides all forms of glow discharge dc and ac. Therefore it is not surprising that during measurements of the corona discharge in CO and its mixtures with H<sub>2</sub> and H<sub>2</sub>O dark-coloured deposits were formed on the inner electrode of a coaxial system for the corona discharge at both polarities. The first deposit (positive corona discharge in CO) was analysed by IR absorption spectrometry. It turned out to be a highly conjugated polymer instead of pyrolytic carbon [2]. This fact has led to the decision to study the structural composition of

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substances formed in a similar way in discharge of both polarities in CO and its mixtures, as well as to compare them with polymers of a similar type.

### II. EXPERIMENTAL

The experimental apparatus applied was the same as in [2]. It consisted of: 1) a cylindrical corona discharge tube, 2) an electrical circuit illustrated in Fig. 1, 3) a vacuum system represented in Fig. 2, 4) auxiliary devices — a Carl Zeiss UR-10 spectrometer and a Perkin Elmer PE 180.

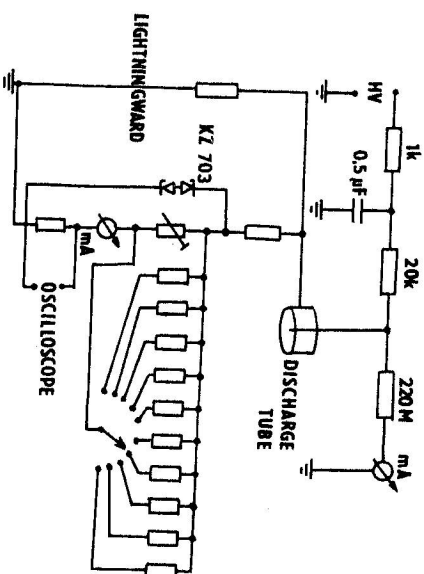


Fig. 1. Scheme of the electrical circuit: HV — high voltage source, a resistance 220 M with mA is used for measuring the high potential. Switch with resistances and KZ 703 is used as an overload protection of the mA. Discharge tube — cylindrical configuration of electrodes: radius of inner electrode (0.1 mm of Mo or Au/Pd 60/40; radius of outer electrode 12.5 mm; length 1 m; material is stainless steel.

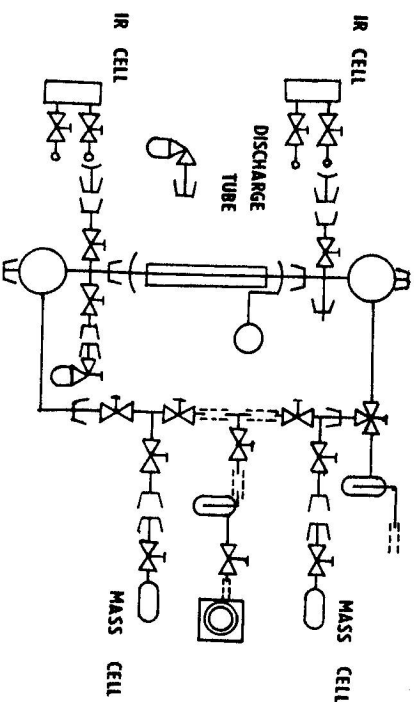


Fig. 2. Scheme of the vacuum system.

The gases CO, H<sub>2</sub> were applied in the technical grade. The main contaminant of CO was Fe(CO)<sub>5</sub>, determined from IR absorption spectra at 720, 800, 2010, 2030 cm<sup>-1</sup>[3, 4]. On introducing the CO into the apparatus the Fe(CO)<sub>5</sub> was frozen out. After the two components had been introduced, the measurement had to be

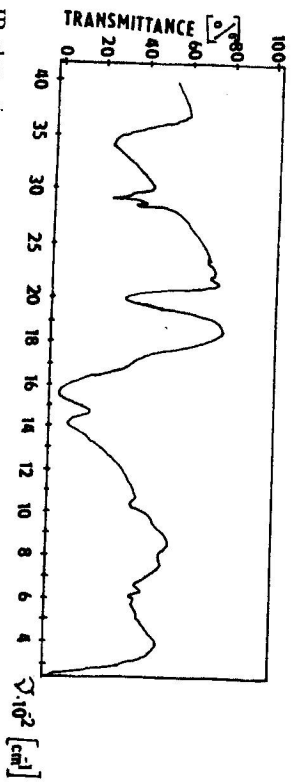


Fig. 3. IR absorption spectrum of the solid deposit on the wire in the case of the positive corona discharge in CO. The most important peaks are:

- deformation vibration O—M of metal chelates, deformation vibration of COO<sup>-</sup>;
- 1410 cm<sup>-1</sup> —  $\nu_2$  COO<sup>-</sup>,  $\nu$  C=O of metal chelates;
- 1560 cm<sup>-1</sup> —  $\nu_{as}$  COO<sup>-</sup>,  $\nu$  C=O of metal chelates;
- 1580—1640 cm<sup>-1</sup> —  $\nu$  C=C conjugated,  $\nu$  C=C of metal chelates;
- 2000 cm<sup>-1</sup> —  $\nu$  C≡O in the case of a CO ligand,  $\nu$  C=O chemisorbed on the surface;
- 2850 cm<sup>-1</sup>, 2920 cm<sup>-1</sup> —  $\nu$ CH<sub>2</sub>;
- 2400—3600 cm<sup>-1</sup> —  $\nu$ OH.

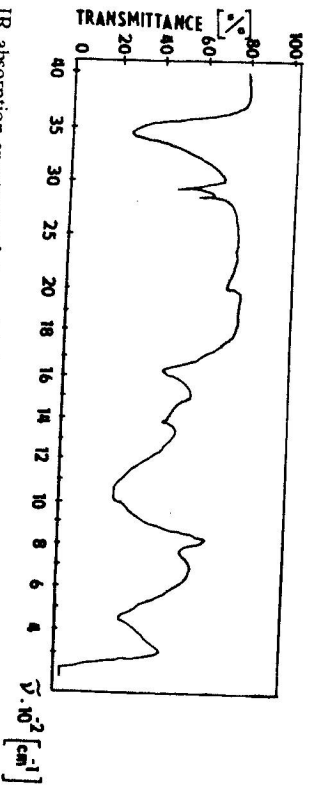


Fig. 4. IR absorption spectrum of the solid deposit on the wire in the case of the negative corona discharge in CO. The most important peaks are:

- deformation vibration O—M of metal chelates;
- 1040 cm<sup>-1</sup> —  $\nu$  C—O—C,  $\nu$  C—OH,  $\nu$  C—C of diketons,  $\beta$ OH;
- 1410 cm<sup>-1</sup> —  $\nu$  C=O of metal chelates;
- 1630 cm<sup>-1</sup> —  $\nu$  C=C conjugated,  $\nu$  C=C of metal chelates;
- 1720 cm<sup>-1</sup> —  $\nu$  C=O,
- 2850 cm<sup>-1</sup>, 2920 cm<sup>-1</sup> —  $\nu$ CH<sub>2</sub>,
- 3440 cm<sup>-1</sup> —  $\nu$ OH.

postponed for about 24—48 hours to create a homogeneous mixture in the apparatus. With every mixture the same total pressure 87 kPa was maintained, and the discharge was in action approximately for 60 minutes. At both polarities of the discharge first of all the V-A characteristic was measured and a proper working point fixed to which we adhered during the measurements. At regular intervals the changes in voltage, current, pressure, design of the discharge and the temperature of the outer electrode were controlled. Before finishing the measurement a sample of gas filling was taken out for scanning the IR absorption spectrum to determine the change in the composition of the gas mixture. After removing the gas sample the apparatus was evacuated and filled with air. Then it was opened to take out the inner electrode, on which the dark deposit with a thickness of some  $\mu$ m had been formed. This deposit was shaved off the wire with activated KBr in a vibration mill. The obtained sample was tabulated and scanned by an IR absorption spectrometer.

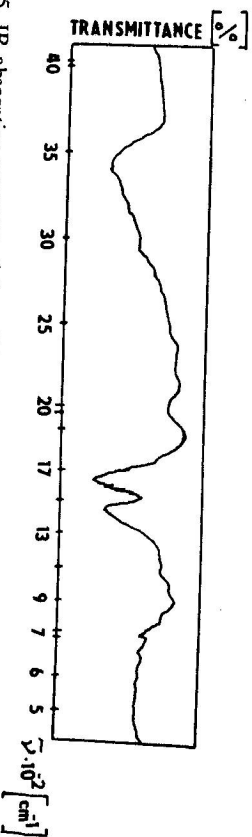


Fig. 5. IR absorption spectrum of the solid deposit on the wire in the case of the positive corona discharge in a CO + H<sub>2</sub>O mixture. The most important peaks are:

- deformation vibration of COO<sup>-</sup> deformation vibration of O—M of metal chelates;
- 1050 cm<sup>-1</sup> —  $\nu$  C—O—C,  $\nu$  C—OH,  $\beta$ OH;
- 1400 cm<sup>-1</sup> —  $\nu_2$  COO<sup>-</sup>,  $\nu$  C=O;
- 1600 cm<sup>-1</sup> —  $\nu_{as}$  COO<sup>-</sup>,  $\nu$  C=C conjugated,  $\nu$  C=C of metal chelates;
- 1680—1740 cm<sup>-1</sup> —  $\nu$  C=C conjugated,  $\nu$  C=C, C=O conjugated;
- 2020 cm<sup>-1</sup> —  $\nu$  C=O of metal chelates,  $\nu$  C=C, C=O conjugated;
- 2850 cm<sup>-1</sup>, 2920 cm<sup>-1</sup> —  $\nu$ CH<sub>2</sub>;
- 3430 cm<sup>-1</sup> —  $\nu$ OH;

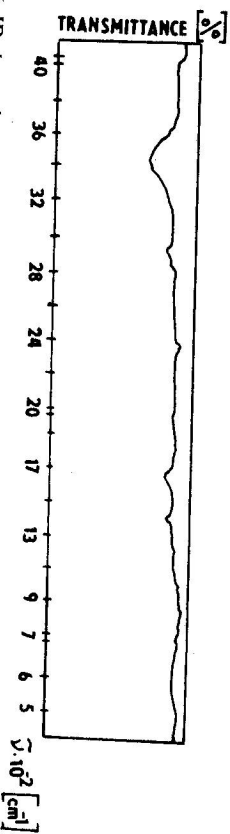


Fig. 6. IR absorption spectrum of the solid deposit on the wire in the case of a negative corona discharge in a CO + H<sub>2</sub> mixture. The peaks are very weak. The observed peaks are the same as in the case of the positive corona discharge in a CO + H<sub>2</sub> mixture.

### III. RESULTS

A number of measurements was carried out in a corona discharge of both polarities and in the following mixtures: CO, CO + H<sub>2</sub>, CO + H<sub>2</sub>O. In all cases an Mo wire with a diameter of 0.2 mm was used except in the case of a negative corona discharge in a CO + H<sub>2</sub>O mixture where a Au/Pd wire of the same diameter was used. In the latter case no deposit was formed on the electrode. The IR absorption spectra of all samples obtained with spectrometers the UR-10 and PE 180 are in Figs. 3, 4, 5, 6, 7. For the interpretation of the IR absorption spectra mainly references [5—10] were used.

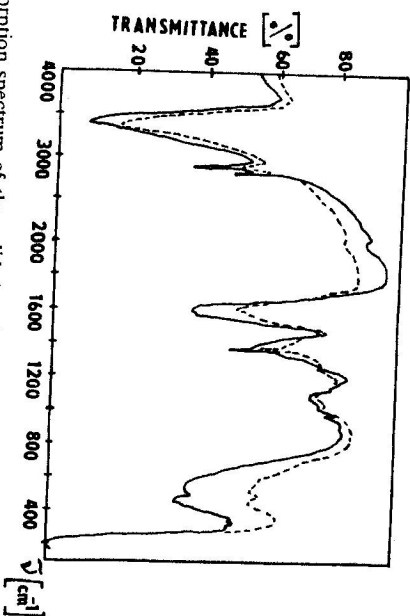


Fig. 7. IR absorption spectrum of the solid deposit on the wire in the case of the positive corona discharge in a CO + H<sub>2</sub> mixture (1:1) — from the upper part of the wire, — from the lower part of the wire. The observed peaks are:

530—560 cm <sup>-1</sup>	— deformation vibration of CCO;
620—670 cm <sup>-1</sup>	— deformation vibration of OCO;
530—670 cm <sup>-1</sup>	— deformation vibration of O—M of metal chelates;
1020 cm <sup>-1</sup>	— vC—O—C;
1120 cm <sup>-1</sup>	— v=C—O—R;
1380 cm <sup>-1</sup>	— deformation vibration of CH <sub>2</sub> —CO—CH <sub>2</sub> ;
1400 cm <sup>-1</sup>	— v, COO <sup>-</sup> ;
1460 cm <sup>-1</sup>	— vC=O of metal chelates;
1580 cm <sup>-1</sup>	— v <sub>as</sub> COO <sup>-</sup> , vC=O of metal chelates;
1630 cm <sup>-1</sup>	— vC=C conjugated, vC=C of metal chelates, vC=C, C=O conjugated;
1720 cm <sup>-1</sup>	— vC=O;
2860 cm <sup>-1</sup> , 2920 cm <sup>-1</sup>	— vCH <sub>2</sub> ;
3440 cm <sup>-1</sup>	— vOH.

### IV. DISCUSSION

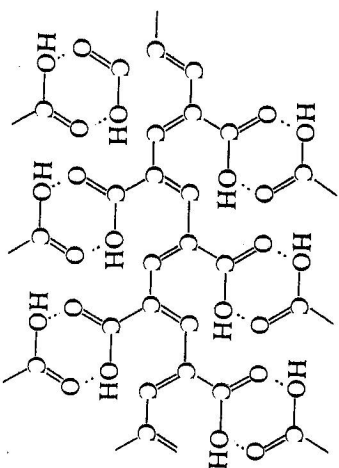
From the measured spectra of the solid deposit the following conclusions have been drawn: On the surface of the Mo inner electrode a layer of a highly

conjugated polymer has been formed. The layer has a thickness of some μm up to tens of μm. According to the polarity of the applied corona discharge and the composition of the introduced mixture the character of the polymer is as follows:

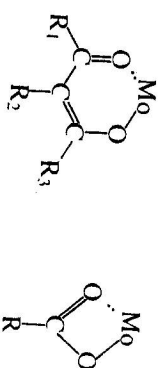
#### POSITIVE CORONA DISCHARGE

With a negligible hydrogen content, i.e. in a reaction of CO gas without contaminants a mixture of polymer substances is formed. The following structural types of polymer deposit are dominating:

1) a conjugated system C=C with a dimer carboxylic acid (or its ester) bound to branch carbon chains, causing additional crosslinking



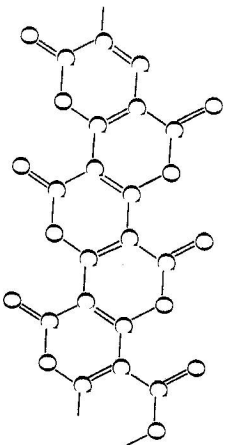
2) compound of metal chelates type based on Mo with ligands of the type C≡O (Mo(CO)<sub>6</sub>) prevailing less of the type of β-dicarboxylic compound. With increasing hydrogen concentration mixtures CO + H<sub>2</sub>O; CO + H<sub>2</sub> — the first component of the mixture markedly decreased (containing a dimer of carboxylic acid) and in the second component there is a decrease of ligands of the C≡O type and an increment of ligands of the type of β-dicarboxylic compounds. The metal chelate on the Mo base has the following structure:



#### NEGATIVE CORONA DISCHARGE

In CO without contaminants in the case of the negative corona discharge the following types of polymer deposit structure dominate:

1) a polymer structure containing cumulative lactone rings with one oxygen heteroatom



The given structure is in good accordance with the structure described in [11—13].  
2) a compound of the metal chelate type, as in the positive corona discharge.

With increasing  $H_2$  concentration in the introduced gas filling the same changes occurred in the negative corona discharge as in the positive one. In the negative corona discharge a smaller amount of sample was observed on the whole in comparison with the positive one. It is explained by a loss of polymer due to bombardment of the negative corona electrode by positive ions, causing destruction of the deposit.

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