# CHEMICAL REACTIONS IN THE CORONA DISCHARGE IN CO AND ITS MIXTURES[1])

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The chemical reactions in the corona discharge in CO and its mixtures with $H_2O$, $H_2$, $N_2$ for decreasing the concentration of CO were investigated. The reaction $CO+H_2$ yielded the best result, since there the drop of the concentration of CO has the value of 50 % through the synthesis of $CO_2$, $CH_4$, organic acids and aldehydes. In the reaction $CO+N_2$ no cyanides occurred.

## ХИМИЧЕСКИЕ РЕАКЦИИ В КОРОННОМ РАЗРЯДЕ, ПРОИСХОДЯЩЕМ В УГЛЕКИСЛОМ ГАЗЕ И ЕГО СМЕСЯХ С $H_2O$, $H_2$, $N_2$

В работе проведено исследование химических реакций в коронном разряде, происходящем в углекислом газе и его смесях с $H_2O$, $H_2$, $N_2$ с уменьшающейся концентрацией CO. Реакция $CO+H_2$ дала самые лучшие результаты, так как в этом случае надение концентрации CO достигает 50 % из-за синтеза $CO_2$, $CH_4$, органических кислот и альдегидов. В реакции $CO+N_2$ не наблюдались никакие цианиды.

## I. INTRODUCTION

In the past few years great attention has been paid to the study of elementary processes and chemical reactions taking place in low temperature plasma. Plasma devices creating place in low temperature plasma. Plasma devices created unusual conditions, that is why some reactions impossible under usual conditions can be carried out with the help of these devices. One of the discharges burning under atmospheric pressure is the corona discharge. As shown in [1] the negative corona discharge acts on the exhaust gases of motorcars so that the concentration of polycyclic aromatic hydrocarbons, which are contained in the exhaust gases, decreases. This leads to the possibility of using the corona discharge for a decrease

[1]) Contribution presented at the 3rd Symposium on Elementary Processes and Chemical Reactions in the Low Temperature Plasma in Krpáčovo, September 22—26, 1980.

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of the CO concentration in exhaust gases. Investigating this possibility we performed experiments studying the behaviour of CO, $CO_2$ and the mixtures $CO+H_2$ and $CO+H_2O$ in the corona discharge of both polarities.

## II. EXPERIMENTS

A positive and negative corona discharge in CO and its mixtures $CO+H_2$ and $CO+H_2O$ were investigated in a discharge tube 1 m long with a cylindrical arrangement of electrodes. The outside cylinder electrode with a diameter of 25 mm was of steel, the inside electrode was of a Mo, resp. Au/Pd 60/40 wire of a 0.2 mm diameter. The discharge tube had a vertical orientation during measurements. The corona discharge had a 70 kV high voltage source with a maximum current of 10 mA. The apparatus was complemented by a vacuum part, which made it possible to evacuate the discharge tube, filling the liquid up to the pressure of saturated vapour, filling up two gases simultaneously, frozen of the reaction products in a vacuum trap that could be closed and making the extraction of gas samples into the two IR absorption cells on both ends of the discharge tube possible. A more detailed description of the apparatus is in [2].

The positive corona discharge in the investigated mixtures remains stable even in $CO_2$ and the mixture of $CO+H_2$. When solid reaction products occurred on the inside electrode, the positive corona discharge current showed a tendency to decrease. The current of the negative corona discharge in all the studied mixtures increases more rapidly than the positive corona discharge current, sometimes it increased rapidly also at a constant voltage. In the case of CO and some mixtures we observed hysteresis while measuring I—V characteristics. The current of the negative corona discharge in technical $CO_2$ began to increase rapidly after the switching on the discharge, it burnt for a relatively short time and a total breakdown with a rupture of the wire electrode occurred immediately. The observed I—V characteristics are analogical to those in [2].

Studying the elementary processes and chemical reactions taking place between the electrodes of the corona discharge directly is very complicated. That is the reason why we have analysed with the help of the IR absorption spectrometry only the gas reaction products forming in the studied gas mixtures induced by the corona discharge. From the results of the product analysis we can conclude on the corona discharge activity taking place in the gas medium between the electrodes. Gas reaction products have been introduced into evacuated IR cells immediately after switching off the corona discharge. We have used 10 cm long cells with windows from an NaCl resp. a KBr single crystal. Samples gained in this way have been analysed with the help of spectrometers UR-10 of Zeiss and Perkin Elmer 180 in VÚKI Bratislava. IR absorption spectra of the samples after the positive and negative corona discharge activity are in Figs. 1—8.



## III. DISCUSSION

The results obtained from analysis of the IR absorption spectra of the investigated samples are in Table 1. It seems that from the obtained results the following conclusions can be deduced as regards the possible use of the corona discharge for decreasing the CO concentration in exhaust gases.

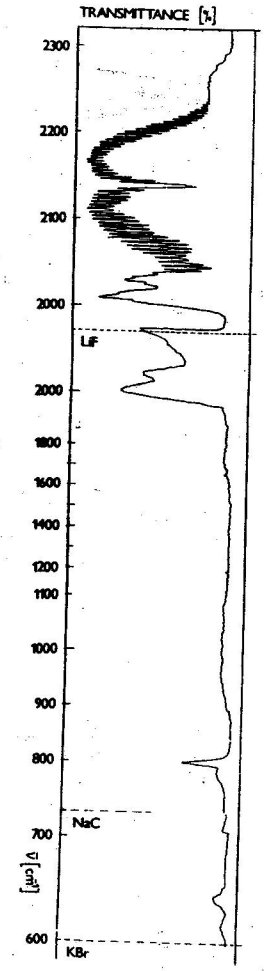


Fig. 1. IR absorption spectrum of CO after the action of the negative corona discharge.

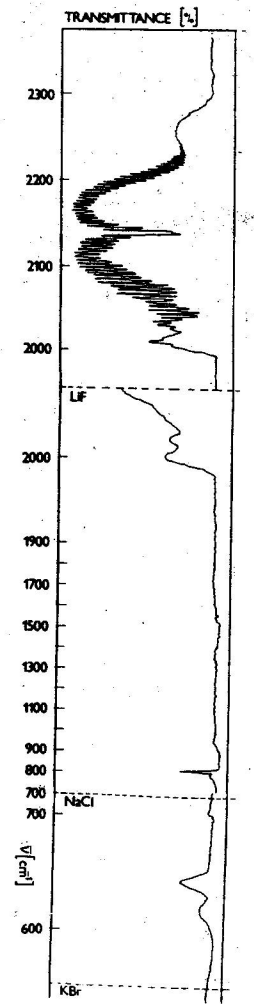


Fig. 2. IR absorption spectrum of CO after the action of the positive corona discharge.

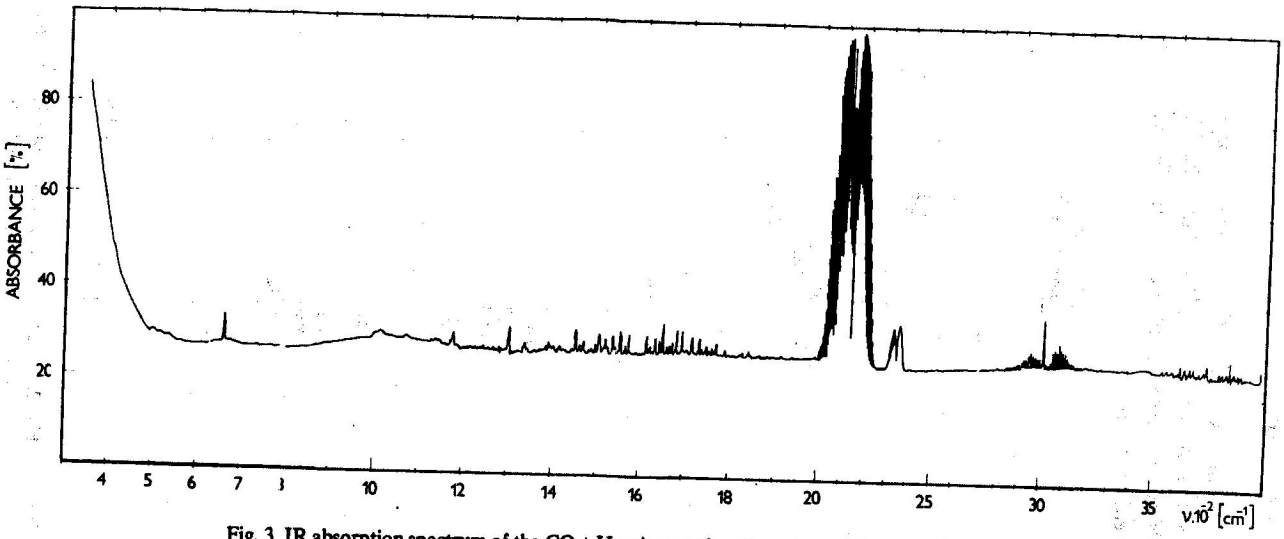


Fig. 3. IR absorption spectrum of the CO + $H_2$ mixture after the action of the negative corona discharge.

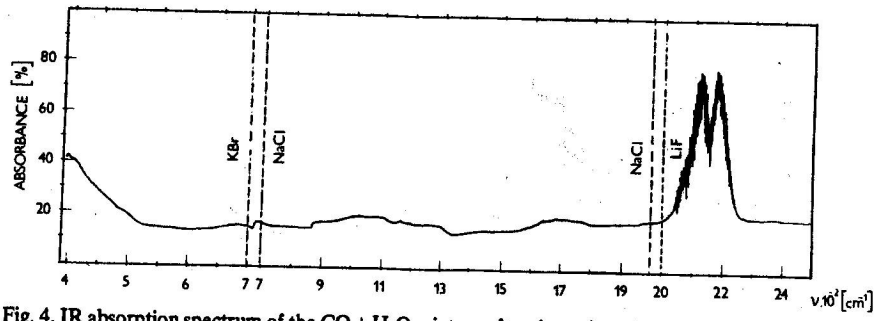


Fig. 4. IR absorption spectrum of the CO + $H_2O$ mixture after the action of positive corona discharge.

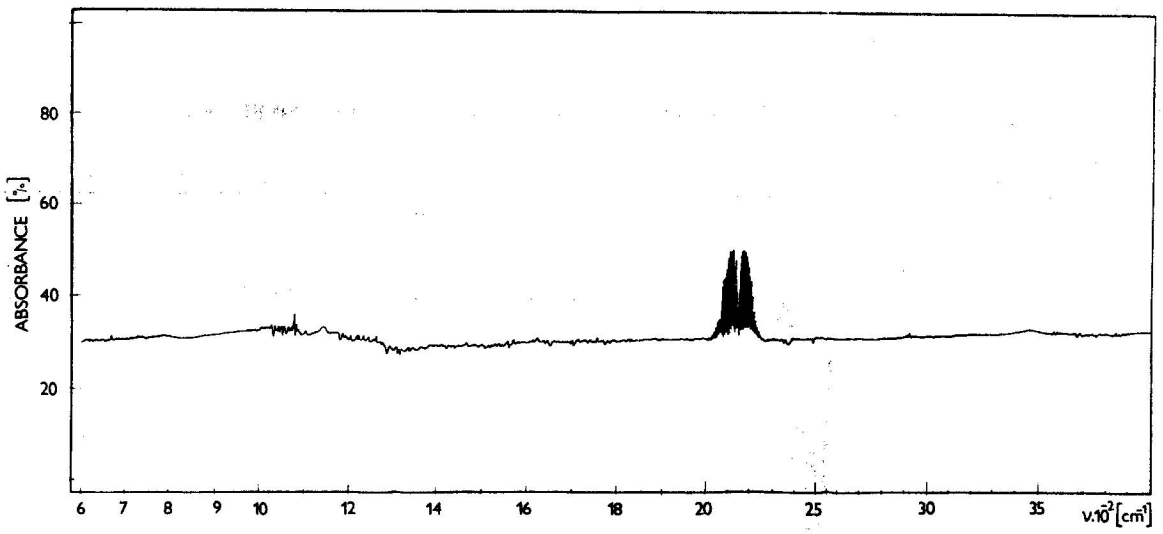


Fig. 5. IR absorption spectrum of the CO + $H_2O$ mixture after the action of the negative corona discharge.

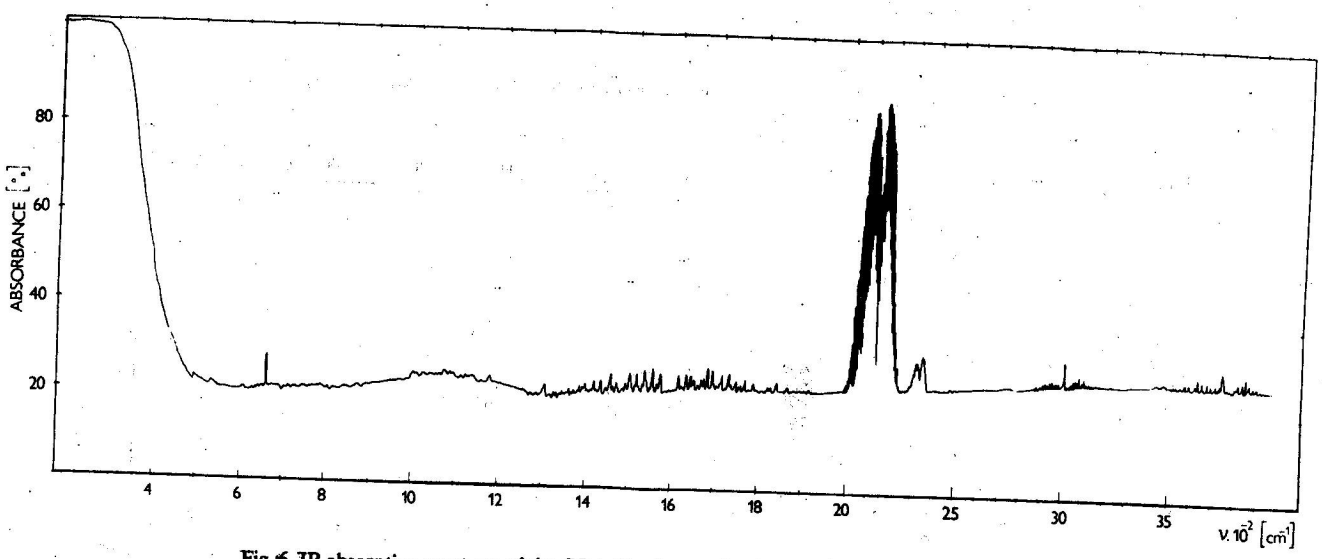


Fig. 6. IR absorption spectrum of the $CO + H_2$ mixture after the action of the positive corona discharge.

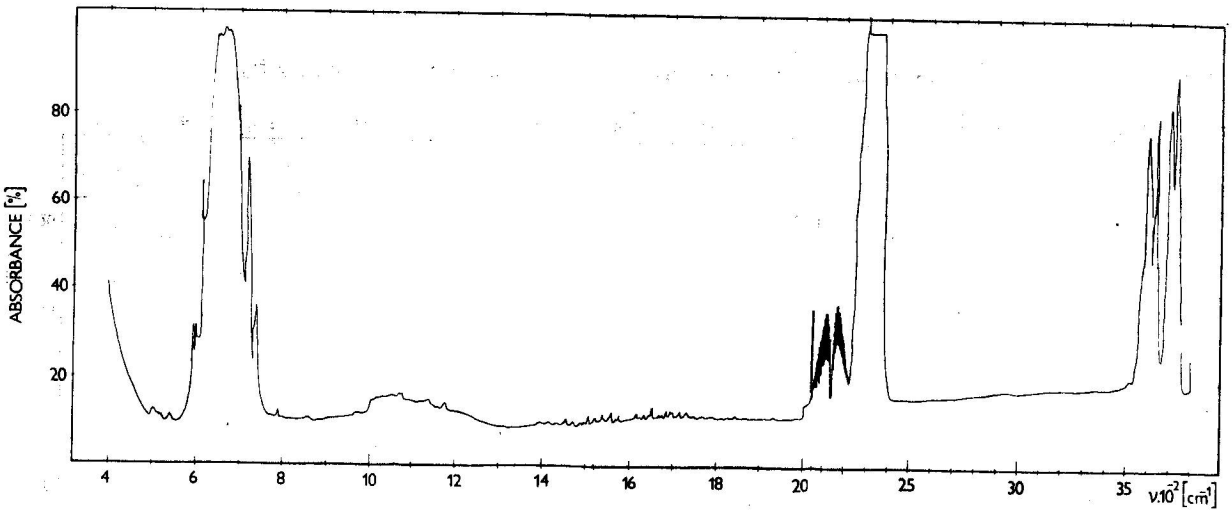


Fig. 7. IR absorption spectrum of $CO_2$ after the action of the negative corona discharge.

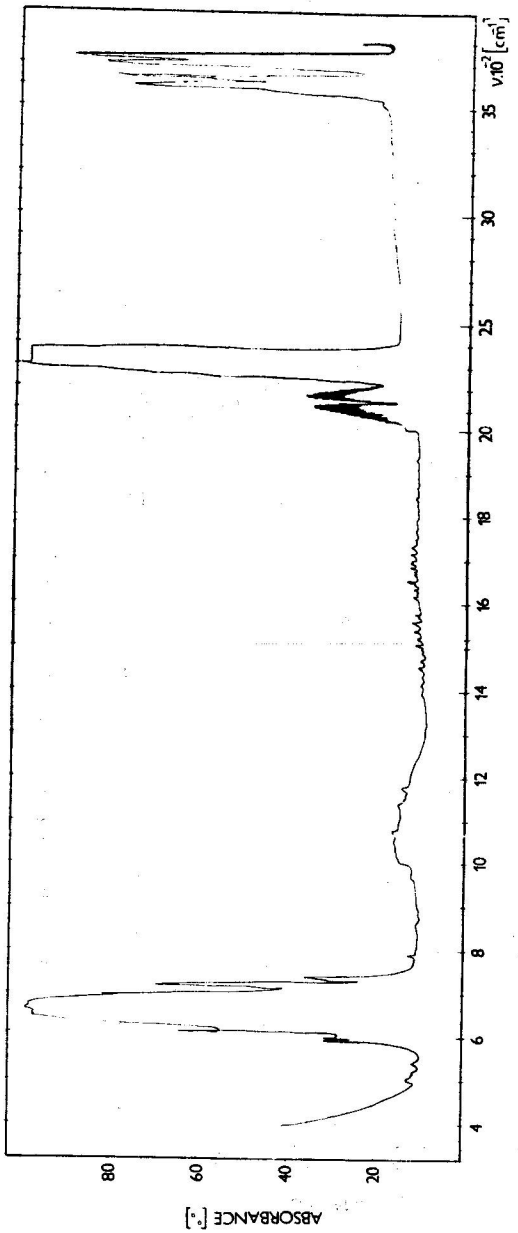


Fig. 8. IR absorption spectrum of $CO_2$ after the action of the positive corona discharge.



1) For a decrease of the CO concentration it seems advantageous to mix it with hydrogen while the positive and the negative corona discharge in the mixture of $CO + H_2$ in a 1 : 1 ratio leads to a decrease of the CO concentration up to 50 % and all the introduced hydrogen is consumed in forming reaction products ($CH_4$, $CO_2$, aldehydes, ketones, organic acids). It is possible that in a mixture with a 1 : 3 or 1 : 4 ratio the decrease of the CO concentration in the mixture would be considerably greater. The results are the same in both polarities of the discharge.

2) From the practical point of view it would be convenient to mix CO with water vapour. In our experiments in a $CO + H_2O$ mixture the pressure of water vapour

Table 1

The results of positive and negative corona discharge acting on CO, $CO_2$, $CO + H_2$, $CO + H_2O$

| Filling | Polarity of discharge | Characteristical frequencies of result sample from IR absorption spectra |
|---|---|---|
| CO | + | 620, 645, 2260 $cm^{-1}$ — $CO_2$ |
| | | 780, 800, 2020 $cm^{-1}$, — $Fe(CO)_5$ contamination |
| | | 2000—2200 $cm^{-1}$ — CO |
| CO | − | 620, 645, 2260 $cm^{-1}$ — $CO_2$ |
| | | 780, 800, 2020 $cm^{-1}$ — $Fe(CO)_5$ contamination |
| | | 2000—2200 $cm^{-1}$ — CO |
| $CO—H_2O$ | + | 645 $cm^{-1}$ — $CO_2$ |
| | | 2000—2200 $cm^{-1}$ — CO |
| $CO—H_2O$ | − | 645 $cm^{-1}$ — $CO_2$ |
| | | 900—1300 $cm^{-1}$ — group C—O—C, def. C—OH |
| | | 1600—1800 $cm^{-1}$ — group C=O |
| | | 2000—2200 $cm^{-1}$ — CO |
| $CO—H_2$ | + | 670, 2340, 2370 $cm^{-1}$ — $CO_2$ |
| | | 1305, 1530, 2900—3160 $cm^{-1}$, — $CH_4$ |
| | | 1350 $cm^{-1}$ — plane def.—$CH_3$—CO—$CH_3$ |
| | | 1440, 1650 $cm^{-1}$ — sym. and antisym. val. $COO^-$ |
| | | 1740 $cm^{-1}$ — group —C=O |
| | | 2000—2200 $cm^{-1}$ — CO |
| | | 3500 $cm^{-1}$ — out of plane def. —OH |
| $CO—H_2$ | − | 670. 2340, 2370 $cm^{-1}$ — $CO_2$ |
| | | 1305, 1530, 2900—3160 $cm^{-1}$ — $CH_4$ |
| | | 1350 $cm^{-1}$ — plane def. $CH_3$—CO—$CH_3$ |
| | | 1440, 1650 $cm^{-1}$ — sym. and antisym. val. $COO^-$ |
| | | 1740 $cm^{-1}$ — group —C=O |
| | | 2000—2200 — CO |
| | | 3500 $cm^{-1}$ — out of plane def. — OH |
| $CO_2$ | + | 667, 2340, 2370 $cm^{-1}$ — $CO_2$ |
| | | 2000—2200 $cm^{-1}$ — CO |
| $CO_2$ | − | 667, 2340, 2370 $cm^{-1}$ — $CO_2$ |
| | | 2000—2200 $cm^{-1}$ — CO |

| Pressure of introduced gases | Composition of result sample | Quantity of sample components |
|---|---|---|
| CO — 87.8 kPa | $CO_2$ | 5 % |
| | $Fe(CO)_5$ | 5 % |
| | CO | |
| CO — 87.8 kPa | $CO_2$ | 1—2 % |
| | $Fe(CO)_5$ | 5 % |
| | CO | |
| CO — 87.8 kPa | $CO_2$ | trace quantity |
| $H_2O$ — 0.2 kPa | CO | |
| CO — 87.8 kPa | $CO_2$ | trace quantity |
| $H_2O$ — 0.2 kPa | CO | |
| | ethers, aldehydes, ketones, organic acids | trace quantities |
| CO — 36.5 kPa | $CO_2$ | 20 % |
| $H_2$ — 36.5 kPa | $CH_4$ | 20 % |
| | CO | 50 % |
| | aldehydes, ketones, organic acids | together 10 % |
| CO — 36.5 kPa | $CO_2$ | 20 % |
| $H_2$ — 36.5 kPa | $CH_4$ | 20 % |
| | CO | 50 % |
| | aldehydes, ketones, organic acids | together 10 % |
| $CO_2$ — 87.8 kPa | $CO_2$ | |
| | CO | 30 % |
| $CO_2$ — 87.8 kPa | $CO_2$ | |
| | CO | 3—4 % |

reached the pressure of saturated vapour at 20 °C, i.e. 0.2 kPa. Many reaction products with a low extinction coefficient in the IR region cannot manifest themselves sufficiently in the IR absorption spectra of the $CO + H_2O$ mixture. The observed spectrum is similar to the spectrum of the mixture of $CO + H_2$, especially in the 800—1900 $cm^{-1}$ region but the concentration of the reaction products is one order lower. The small quantity of the reaction products is caused by the small concentration of water vapour. The situation in exhaust gases is different. Their temperature is about 80—100 °C; the saturated vapour pressure of water at this temperature is high; the water is the combustion product and that is why it is in exhaust gases in both stages in a sufficient quantity with a pressure of about 50 kPa. From the point of view of the result utilization of the positive or the negative corona discharge is the same. The negative corona discharge gave a somewhat greater concentration of the reaction products.



3) The behaviour of the corona discharge in pure $CO_2$ causes the reverse dissociation of $CO_2$ to CO in the negative corona discharge to be minimal. Because of this effect the use of the negative corona discharge was given priority as a means for the decrease of the CO concentration in mixtures of $CO + H_2$ with regard to the fact that $CO_2$ is one of the reaction products.

4) The corona discharge used for removing the carbon monoxide from exhaust gases in the same way as it was used for removing the polycyclic aromatic hydrocarbons in the invention No. 178566 would burn on the boundary of air and the exhaust gases. From this point of view the mixture of $CO + N_2$ gains importance. From the IR absorption spectra of the reaction products from the $CO + N_2$ mixture in the corona discharge it resulted that in the mixture cyanides resp. compounds with a nitril group in the gas or liquid state did not occur, which is from the point of view of the application of the corona discharge to exhaust gases the essential criterion.

## REFERENCES

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Received October 20th, 1980