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STUDY OF STRUCTURAL CHANGES IN SURFACE LAYERS OF APPLES DUE TO CORONA DISCHARGE[1])

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The influence of the corona discharge of both polarities on the change in the structure of protective layers of apples was investigated in the atmosphere of air and CO_2 at atmospheric pressure. The qualitative analysis of the protective wax and cellulosic peel of apples was carried out by IR absorption spectroscopy on samples after both natural ageing and effect of the corona discharge.

ИЗУЧЕНИЕ СТРУКТУРНЫХ ИЗМЕНЕНИЙ В ПОВЕРХНОСТНЫХ СЛОЯХ ЯБЛОК, ОБУСЛОВЛЕННЫХ КОРОННЫМ РАЗРЯДОМ

В работе приводятся результаты исследований влияния коронного разряда обеих полярностей в воздухе и в CO_2 при атмосферном давлении на изменения в структуре защитных слоев яблок. Выполнен также качественный анализ защитного материала и клетчатки кожицы яблок на основе спектроскопии инфракрасного поглощения на образцах после естественного старения и после влияния коронного разряда.

I. INTRODUCTION

The solution of the given problem was initiated by information on using ionization to change the stability of foodstuffs [1]. The present work discusses the study of structural changes in surface layers of apples by IR absorption spectroscopy. Two kinds of samples were investigated: the protective apple wax, mechanically removed from the apple surface and the cellulosic peel. The samples were exposed to both the positive and the negative corona discharge in air and CO_2. Several publications [2, 3] describe the origin of active particles formed in discharges in the atmosphere of air and CO_2, less attention is paid to their effect on the change in the material structure.

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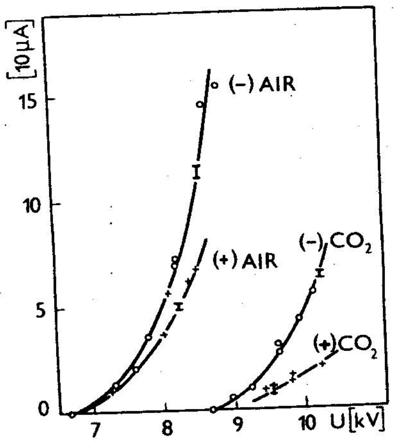
II. METHODS

The experimental apparatus, used for generating the corona discharge, consisted of an electrode system for the corona discharge, an electrical unit and a vacuum unit. The latter is shown in Fig. 1. The HT electrode was created from a system of 18 planar W wires, with a total length of 1.8 m and 0.1 mm in diameter. Within a variable distance (in the case of our measurements 10 mm), in parallel with the plane of the wires a brass electrode was mounted, carrying the sample. A pulse generator of both polarities, externally filtered, served as the HT source. The volt-ampere characteristics of a corona discharge are given in Fig. 2., where the working values are marked by the abscissa. The acting period of the discharge was in the range of 50—60 min.



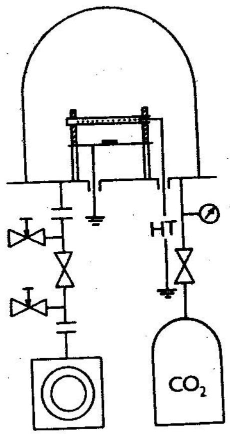


Fig. 1. Diagram of the apparatus for generating the corona discharge.

Fig. 2. Volt-ampere characteristics of the corona discharge.

The sample structure was identified from IR absorption spectra scanned from the following spectrometers: PE-180 with the range of 4000—400 cm^{-1}, and UR-10 within the range of 5000—400 cm^{-1}. The samples for spectrum scanning were prepared by the KBr tabletting technique on using a microilluminator.

III. STRUCTURE OF THE INVESTIGATED SAMPLES

Natural vegetable waxes have the structure of esters of higher fatty acids with monofunctional alcohols. They represent a mixture of esters, the individual components of which are difficult to separate.

The substantial part of peels consists of vegetable tissue, i.e. cellulose. It is a non-reducing poly-saccharide, highly resistant against environmental effects.

IV. IR SPECTROSCOPY ANALYSIS OF THE STRUCTURE OF THE INVESTIGATED SAMPLES

The structure of the given products was characterized on the basis of groups present in the IR spectrum. The absorption bands were coordinated empirically according to literature [4, 5]. From the changes in the IR spectrum the stable changes, arisen in the structure due to the disdharge, were evaluated.

Fig. 3 shows the spectra (in the range 2000—700 cm^{-1}) of apple wax in the orignal state (1), after the action of the positive (2) and the negative corona discharge generated in air (3). On comparing the spectra it can be seen that the wax structure is changed in both cases. The decrease of the absorption band of the $\nu C=O$ esters groups is the most marked in the region of 1740 cm^{-1}.

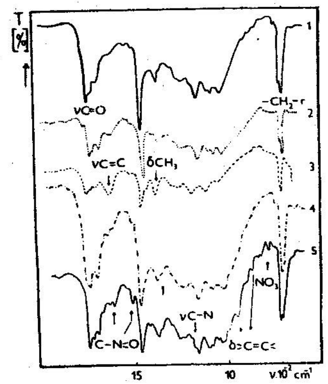


Fig. 3. IR spectra of apple wax: (1) in the original state; (2) after the action of the (+) discharge in air; (3) after the action of the (−) discharge in air; (4) after the action of the (+) discharge in CO_2; (5) after the action of the (−) discharge in CO_2.

In a positive corona discharge the decrease of esters band is due to the hydrolytic destruction to acids and alcohols. In the spectrum there is an increase of the absorption band of the $\nu C=O$ dimers of aliphatic acids and the $\nu_{as}C-O$ acids in the region of 1690 cm^{-1} and 1270 cm^{-1}, respectively.

With a negative corona discharge the absorption band increase is the region of 1650 cm^{-1}, in evidence of the growth of nitrate groups ($-ONO_2$). The absorption band in the region of 1370 cm^{-1} can be interpreted as a growth of CH_3 groups (these can be formed at a chain scission), as well as by a symmetrical vibration of the nitro-groups ($-NO_2$).

With a positive corona discharge in CO_2 (4) the minimum change was in the absorbance of the ester band. An increase of the absorption bands of the C–O–C bonds has been observed. These bonds can be produced by crosslinking reactions.

With a negative corona discharge in CO_2 the loss of the absorption band of ester groups is also lower than in air. The growth of absorption is marked in the region of 1620—1650 cm^{-1} and 1530 cm^{-1}, being probably connected with the formation of secondary amides of acids (–CONH). It can be admitted, as the technical grade CO_2 contains air, too. In the region of 960—880 cm^{-1} there are increasing absorption bands of deformation vibrations double bonds which prove degradation processes.

Both the positive and the negative corona discharge was appled also to apple peels. The spectroscopically observed structural changes were not sufficiently marked.

V. CONCLUSION

With a forced ionization of air [2], ozone and nitrogen oxides can be considered as the most reactive formations. The negative ions of oxygen are apt to take part in crosslinking reactions by linking to double bonds, but after longer action they cause a scission of bonds. In the primary stage a corona ddischarge in air generates nitrogen oxides, apt to react with a hydrocarbon chain and create a stable groups of esters of nitrid acid [6].

With forced ionization in the positive and the negative corona discharge in the atmosphere of CO_2 various types of ions are formed: CO^+, O^+, O_2^+, CO_2^+, CO_3^-, CO_4^-, which are able to create complex ions.

For evaluating the structural changes in apple wax we give the ratio of absorbances of ester band to the correlation band of the CH_2 chain in all the compared samples (marking as in Fig. 3):

	1	2	3	4	5
$A_{C=O}/A_{CH_2}$	0.89	0.61	0.51	0.81	0.69

It is evident that the minimum degradation of ester occurs with a positive corona discharge in the atmosphere of CO_2, the maximum degradation with a negative corona discharge in air.

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