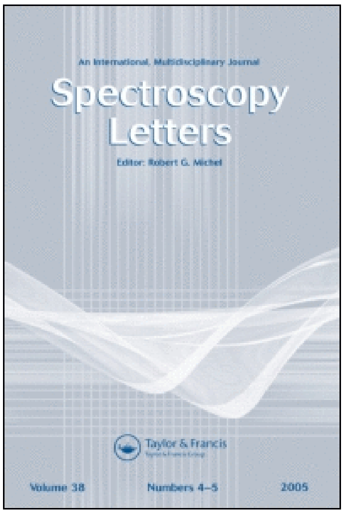

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Structural Changes During the Silica Rubber Filler Precipitation Investigated by IR and NIR Spectroscopy

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STRUCTURAL CHANGES DURING THE SILICA RUBBER FILLER PRECIPITATION INVESTIGATED BY IR AND NIR SPECTROSCOPY

KEY WORDS: Silica rubber fillers, i.r. and n.i.r. spectra

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INTRODUCTION

Different kinds of silicic acids have been proved to have different properties in the infra red and near infra red[1-2/]. Precipitated white rubber fillers similarly as the pyrogenic Aerosil differ from silica gels by sharper and more intensive Si-O bands in the infra red, which may be explained by a higher periodicity of structure[1/]. In dry CCl_4 Aerosils and precipitated silica rubber fillers form a permanent, more or less transparent suspension, whereas the silica gel particles drop to the bottom. The suspension of silicic acids gives a distinct spectrum of OH bands in the near infra red.
The value of the background level of this spectrum points to smaller or bigger particle seizes. Thus the background absorption of the pyrogenic Aerosil is much lower than of other silicic acid fillers[2/].

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The precipitated silica rubber fillers are usually obtained by the neutralization of a sodium silicate solution with sulphuric acid. The nature of the precipitate changes during the precipitation.

The aim of the present work was to study the formation of the white rubber filler Arsil during its precipitation in the industrial process[3/].
Samples were drawn successively from the reaction vessel and their properties determined by methods reported previously[1-2/]. The results of spectroscopic measurements in the IR and NIR were compared with conventional methods used in the analysis of fillers.

EXPERIMENTAL

The precipitation was carried out in two steps, at the temperature 80-85°C[3/]. In the first step lasting 60 min., into the reaction vessel with 4.0 m^3 of water two streams were fed simultaneously, one of a water glass solution of the molar ratio SiO_2/Na_2O = 3,23, containing 0,64 $mol.l^{-1}$ Na_2O and 2,0672 $mol.l^{-1}$ SiO_2, the other of a sulphuric acid solution /0,755 $mol.l^{-1}$/.
The amounts of reagents supplied after a given time are presented in Tab.1.

In the second reaction step, lasting 30 min, the H_2SO_4 supply was continued according to Tab.1. After the end of the reaction the pH was adjusted to 3,2-3,8.
During the whole process, every 10 min., a sample from the reaction vessel was drawn /Tab.1-2, samples 1-9/. The samples were filtered, washed in a centrifuge and dried at 110°C in the laboratory.

Tab.1. The Arsil rubber filler precipitation

The number of sample	Reaction time min	Amount of sodium silicate solution m^3	Amount of sulphuric acid solution m^3	Molar ratio Na_2O/H_2SO_4
1	10	2,93	1,29	1,93
2	20	5,86	2,58	1,93
3	30	8,80	3,87	1,93
4	40	11,73	5,16	1,93
5	50	14,66	6,46	1,93
6	60	17,60	7,75	1,93
7	70		10,13	1,47
8	80		12,52	1,19
9	90		14,90	1,00

Tab.2. The changes of physico chemical properties during the Arsil rubber filler precipitation.

Nr of sample	Apparent bulk density kg/m^3	Linseed oil adsorptivity 3/ g/100g	Areatron spec. surface area. m^2/g	Ignition loss at 1100°C g/100g SiO_2	Background level at 5260cm^{-1} a.u.	Band intensity A_{1100}
2	800	39	14	7,71	-	0,068
3	812	40	18	11,75	-	0,084
5	621	60	32	10,13	-	0,075
6	365	117	61	7,10	-	0,121
7	135	207	71	7,09	0,042	0,391
8	97	253	78	6,91	0,073	0,538
9	70	261	110	5,49	0,412	0,632
10	74	240	111	5,56	0,415	0,676
11	77	235	103	5,98	0,403	0,618

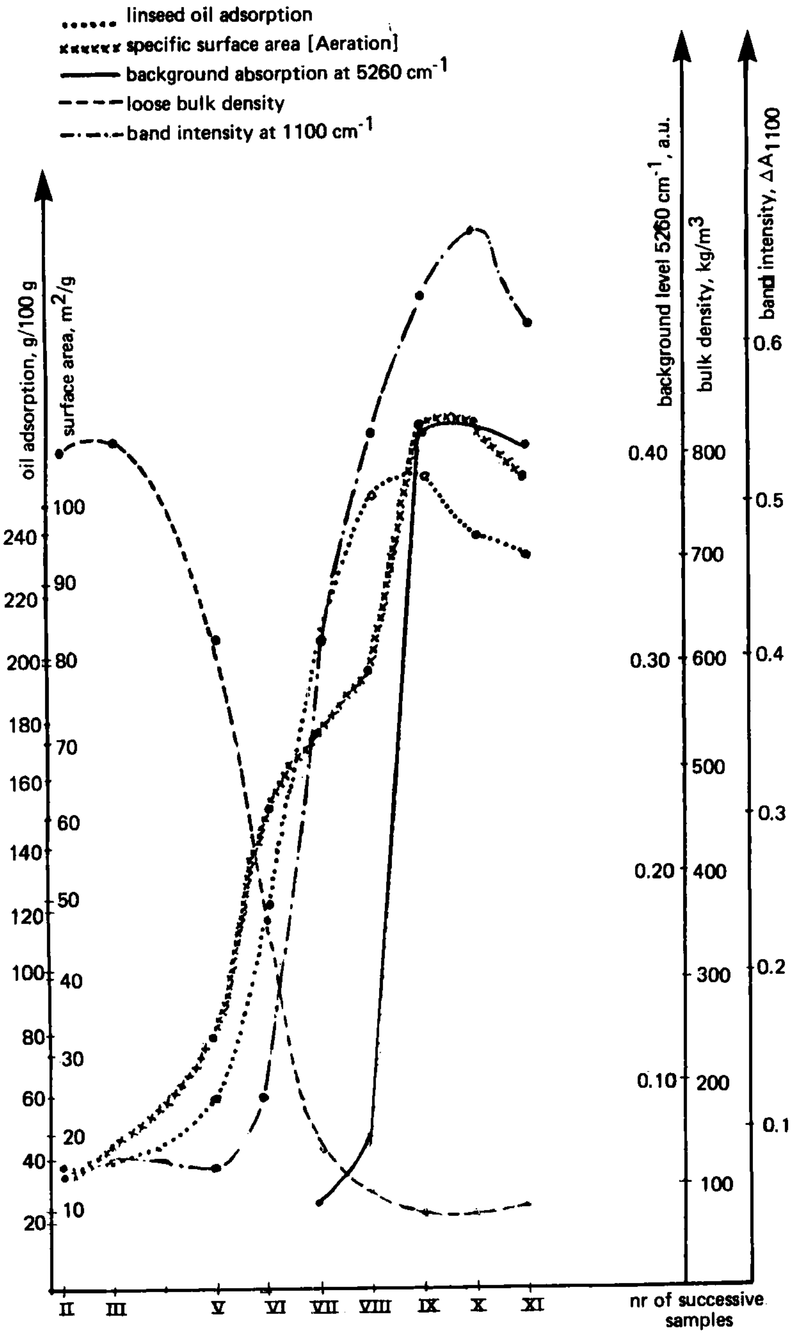

FIG.1. Structural changes of the silicic acid rubber filler during its precipitation

Sample 10 /Tab.2/ was drawn after the industrial filtration and washed and dried in the laboratory. Sample 11 represents the product after the industrial washing at pH 4-4,8 and the subsequent filtration and drying.

The samples were analysed by several methods$^{1-2/}$. The results are shown in Tab.2 and Fig.1. The 1100 cm^{-1} silica band was selected for comparison of IR band intensities measured as absorbance difference by the base line technique$^{1/}$.

To determine the background level of the NIR spectra the predried silica samples were suspended in CCl_4 and their spectra measured on the Unicam SP 700 spectrophotometer$^{2/}$ in the range of 4100-8000 cm^{-1}.

The specific surface area was determined on the automatic analyser Areatron /Leybolt-Heraeus, G.F.R./, basing on the argon adsorption at one point of the BET adsorption isotherm.

The ignition loss at 1100°C was determined on samples predried at 110°C.

RESULTS AND DISCUSSION

As shown in Fig.1 and Tab.2 at the beginning of the precipitation in the alkaline solution a compact, almost non porous mass of very low oil adsorptivity, low specific surface area and very high loose bulk density is formed /samples 2-5/. The silica bands of the IR spectra of these samples are low and broad, sugesting a low structural order$^{1/}$. The samples show a high ignition loss indicating an early condensation state.

The high jump of the oil adsorptivity /porosity/, accompanied by a strong decrease of the bulk density and rise of the IR band intensities between sample 5 and 7 supports the aerlier statements that the increase of structure order of silicas causes a decrease in bulk density and increase of pore volumes[1/].

These changes together with a growth of the specific surface area go on until the end of the neutralization /sample 9/, when a sudden formation of bigger particles is taking place indicated by the jump of the background level of the NIR spectrum.

The easy determinable value of the background level at 5260cm^{-1} characterizes the dispersibility of silica fillers.

In preliminary investigations on different fillers an inverse proportionality between the background level in the NIR and the ability to increase the strength of rubber compounds was found[4/]. Further investigations on the relation between the background level of NIR spectra and quality of silica rubber fillers should be carried out. The ease with which these spectra can be obtained shows bright prospects for NIR examination of silica rubber fillers.

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