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ON THE PROBABLE MECHANISM OF THE INTERACTION OF CARBON BLACK WITH PHENYL-2-NAPHTHYLAMINE AND MERCAPTOBENZOTHIAZOLE (CAPTAX)

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The most reactive part of the surface of carbon-black particles consists of the places where the lateral, prismatic faces of crystallites emerge. Here are also found functional groups connected with the crystal lattice, and unpaired σ- and π-electrons at carbon and oxygen atoms. The complex chemical nature of the surface of carbon blacks affects the character of adsorption of gases and liquids, polymers and rubber ingredients, etc.; the catalytic decomposition of peroxide groupings in rubber molecules and the oxidation of rubbers; the processes of vulcanization and aging of rubbers, etc.

In the present work we investigated the interaction of channel black (from the Ukhta plant) with the rubber antioxidant–phenyl-2-naphthylamine (P2NA)–$C_6H_5—N—C_{10}H_7$, with the vulcanization accelerator mercaptobenzothiazole (captax), known in two tautomeric structures (1), of which I corresponds to its name:

$$(I) \quad \rightleftharpoons \quad (II)$$

and with triphenylmethyl radicals (TPM)–$(C_6H_5)_3C\cdot$.

A sample of carbon black, previously conditioned in vacuum at 250°C to a residual pressure of 10^{-4} mm Hg, was treated with alcoholic solutions of P2NA and captax and with a benzene solution of hexaphenylethane at 20 and 50°C. Destruction of the excess substance was carried out with the same solvents under the same conditions. In the case of P2NA, adsorption and desorption of vapors at 150°C were carried out in the absence of air. Completeness of desorption was checked calorimetrically and interferometrically. The content of proton-donating groupings was determined by a previously described method (2). The accuracy of the determination is 10%.

Investigations by the method of electron paramagnetic resonance (EPR) were carried out on an RÉ-1301 radiospectrometer ($\nu_1 = 9320$ MHz) and on a radiospectrometer with frequency $\nu_2 = 450$ MHz. Measurements were performed at temperatures of 77 and 290°K. The influence of oxygen adsorbed by the surface of the carbon black on the width of the EPR line was eliminated by partial degassing of the carbon-black samples to $5 \cdot 10^{-2}$ mm Hg. A higher vacuum did not affect the line width. The electrical conductivity of the carbon black, which makes it difficult to study the form of the EPR line, was greatly reduced by wetting the carbon black with vaseline oil followed by heating to 370°K. Carbon-black samples prepared in this way were not evacuated and were used for control checks in determining the number of paramagnetic centers, which was carried out at $\nu_3 = 270$ MHz from integral resonance absorption curves (the first moment of the resonance absorption curve).

The number of paramagnetic centers in the carbon black was determined at ν_2 and 290° K for evacuated samples, with line saturation being excluded. In this procedure the EPR line from the carbon-black sample under study in vacuum was compared with the EPR line from polycrystalline α,α-diphenyl-β-picrylhydrazyl (DPPH), mixed in air with an equal weight amount of the carbon black under study (comparison sample—CS).

The measurements were carried out in identical ampoules, each occupying the same position in the generator coil. In this way errors associated with the influence of different losses in the generator circuit were eliminated.

The concentration of paramagnetic centers N per 1 g of carbon black was calculated from the formula

$$N = \frac{M_1 N_0}{M_0 m_1},$$

where M_1 and M_0 are the first moments of the resonance absorption curves for the carbon-black sample under study and the comparison sample with DPPH, respectively; N_0 is the number of paramagnetic centers for the comparison sample; and m_1 is the weight of carbon black in grams. The accuracy of the determination was $\pm 3 \cdot 10^{18}$ paramagnetic particles per 1 g; the g-factor for all the samples studied was 2.003 ± 0.002.

Table 1

Carbon black	A	n_1	n_2	$n = n_1 + n_2$	Δn	N	ΔN	δH, Oe
	absolute amount per 1 g of carbon black $\times 10^{-18}$	absolute amount per 1 g of carbon black $\times 10^{-18}$	absolute amount per 1 g of carbon black $\times 10^{-18}$	absolute amount per 1 g of carbon black $\times 10^{-18}$	absolute amount per 1 g of carbon black $\times 10^{-18}$	absolute amount per 1 g of carbon black $\times 10^{-18}$	absolute amount per 1 g of carbon black $\times 10^{-18}$	
Channel black, serial	–	84	41	125	–	31	–	1.7
Treated with P2NA	26	110	47	157	+32	26	−5	2.9
Treated with captax	71	115	59	174	+49	12	−19	2.9
Treated with TPM	30	84	41	125	0.0	60	+29	1.7

Note. A is the number of irreversibly adsorbed molecules; n_1 is the number of strongly protogenic groups (carboxyls, part of the phenols); n_2 is the number of the remaining protogenic groups; Δn is the change in the total number of protogenic groups; N is the number of paramagnetic centers—unpaired spins; ΔN is the change in the number of paramagnetic centers; δH is the width of the EPR line between the maximum and minimum of the first derivative of the resonance curve.

The results obtained are given in Table 1, from which it follows:

1. Irreversible adsorption of P2NA and captax on channel black leads to an increase in the content on its surface of protogenic groupings, both strong and weak, despite the fact that P2NA is a weak base capable of forming salts with a number of acids. Captax is a neutral substance. In contrast to both of them, adsorption of triphenylmethyl radicals does not cause an increase in the content of protogenic groupings on the carbon black.

2. Irreversible adsorption of P2NA leads to a slight decrease in the number of paramagnetic centers, and the width of the EPR line also changes. The number of protogenic groups formed—$32 \cdot 10^{18}$ per 1 g—is practically equal

to the value of N for the initial carbon black—$31 \cdot 10^{18}$ per 1 g. The number of irreversibly adsorbed P2NA molecules—$26 \cdot 10^{18}$ per 1 g—is equal to the number of paramagnetic centers on the treated carbon black.

3. Irreversible adsorption of captax considerably decreases the number of paramagnetic centers, changing the width of the EPR line in exactly the same way as does adsorption of P2NA. The number of protogenic groups on the carbon black increases sharply.
4. Irreversible adsorption of TPM does not change the width of the EPR line. The increase in the number N by $29 \cdot 10^{18}$ per 1 g is practically equal to the number of adsorbed TPM radicals—$30 \cdot 10^{18}$ per 1 g.

These experimental results may be interpreted as follows. On the surface of carbon blacks there are aroxyl radicals (3);

including semiquinone radicals (^4) and, as was proposed earlier (^2), carboxylate radicals.

Rupture by these radicals of the N—H bond in P2NA and of the S—H bond in captax should lead to the formation of carboxyl and phenolic groupings. The weak radical $C_6H_5(C_{10} - H_7)N^{\bullet}$ that arises in our case is evidently not capable of reactions other than recombination. However, the weak bond of this radical with the equally weak radicals of the carbon-black surface does not give a stable compound. The energy of this bond is evidently less than the total heat q of physical adsorption of the phenyl and naphthyl rings on the carbon-black surface. For the case of the basal plane of graphite, using an additive scheme (^5), one can estimate $q = 134$ kJ/mol, which is undoubtedly higher than the heat of recombination of two very weak radicals. The orientation of the P2NA radical (which has a pyramidal structure) with its aromatic rings lying in one plane relative to the carbon-black surface is more than probable. The nitrogen atom with the unpaired electron faces toward the external medium. Such a scheme explains the equality of the quantities A and N in the case of adsorption of P2NA. The irreversibility of the adsorption must then be regarded as conditional. It is evident that q for adsorption of the P2NA radical on channel black is higher than the heat of its dissolution in alcohol and the heat of sublimation at 150°C.

An essential fact is the presence of polar groupings on channel black and the fact that it is not the P2NA molecule that is adsorbed, but the radical. From the surface of less active blacks, P2NA is desorbed by alcohol.

Captax in alcoholic solution is in tautomeric form I; abstraction of hydrogen gives the radical $RS^{\bullet}$, sufficiently strong to carry on chain reactions in a rubber medium (^6). It may be assumed that this radical is capable of breaking weak C—H bonds on the surfaces of carbon blacks, initiating a chain process of carbon-black oxidation. Chain oxidation of the latter is mentioned in the literature (^3). This process may explain the increase in the number of protogenic groups during the interaction of carbon black with captax in the presence of atmospheric oxygen. A considerable fraction of the captax radicals may recombine with surface radicals arising on the carbon black during its oxidation.

After the interaction of carbon black with captax is completed, free radicals remain on the surface—$12 \cdot 10^{18}$ per 1 g. These radicals are neither semiquinone nor carboxyl, and evidently are not oxygen-containing at all. They cannot be carbon radicals; indeed, the width of the EPR line of channel black deprived of oxygen groupings is different (2.9 oersted). From our point of view, these are radicals of adsorbed captax, present in tautomeric form II, characteristic of the crystalline substance and of its solutions in hydrocarbon at moderate temperatures (⌒1). The unpaired electron then belongs to the nitrogen atom; hence its similarity to the P2NA radical.

As already mentioned, for samples of carbon blacks treated with captax and P2NA, the observed EPR line is due to an unpaired electron (u.e.), localized mainly at the nitrogen atom. From these samples, with the obtained concentration of paramagnetic particles ($\sim 10^{18}$ per 1 g), one could have expected the appearance of a resolved anisotropic hyperfine structure (h.f.s.) caused by interaction of the u.e. with the magnetic moment of the nitrogen-atom nucleus. Such h.f.s. could not be observed, but the EPR line broadened noticeably compared with samples of untreated carbon black (see Table 1).

The absence of an observable h.f.s. and the broadening of the line for samples of carbon blacks treated with captax and P2NA can be explained by assuming that in these carbon blacks there exist microgroups of carbon-black particles possessing unpaired electrons and arranged in very dense packing. Thus, within the microgroups there is a strong exchange interaction, which makes resolution of the h.f.s. difficult, but which is weaker than that observed in untreated carbon black.

Adsorption of TFM radicals undoubtedly also occurs on the phenyl rings, as a result of which the unpaired spin is preserved.

Naturally, here $\Delta N = A$; however, TFM is evidently oxidized with the formation of $(C_6H_5)COO^\bullet$ radicals, similar to the aroxyl radicals of carbon black.

The mechanism described for the interaction of carbon black with two rubber ingredients shows that, beginning with the mixing operation, processes may occur in the rubber compound that change both the nature of the carbon-black surface and the surrounding medium; moreover, the initiator of these processes is the active surface of the carbon black itself.

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Note: Figure translations are in progress. See original paper for figures.