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Preparation of sulfur pigments based on the interaction of sulfur with aniline

Abstract. The article presents the results of obtaining and investigating the various ratios of the components of aniline hydrochloride-S-CaO (Al_2O_3) 1: 0.4: 0.6; 1: 1: 0.6; 1: 2: 10; 1:10:10 – up to ten times the binding of sulfur and oxides to aniline, having a different color range from dark green to light brown, depending on the composition of the components. In sulfurous composites with various molar ratios of sulfur components, which plays the role of an inorganic filler, it binds almost completely, while remaining chemically inert.
Key words: aniline, polyaniline, sulfur, aniline dyes, styrene, ammonium persulfate, acrylic acid, pigments.

Introduction

Polyaniline is synthesized from the inexpensive aniline monomer through a simple oxidative process in aqueous media, meaning the overall process is scalable and relatively inexpensive. The impurities produced are easily washed away with water and alcohols, and the resulting material takes on a brilliant green color, making it a visually appealing material to investigate. One of the most interesting properties of polyaniline is the dependence of its resistivity on the local pH environment, where a small amount of acid or base can produce a resistivity change of 10 orders of magnitude or greater. While polyaniline in its undoped state displays resistivity in the insulating regime, doping with different acids has led to highly conductive materials with recent reports of essentially metallic polyaniline. The combination of highly tunable electronic properties with a facility for nanostructure formation through relatively simple synthetic methods ensures that polyaniline will continue to be of great interest to the materials science community [1].

Idealized formulae of polyaniline at different oxidation and protonation states:

L = leucoemeraldine (closed valence; shell reduced form; benzenoid structure); E = emeraldine (radical cation intermediate form; combination of quinoid and benzenoid structures); P = pernigraniline form (quinoid structure); LH_{8x}, $EH_{8x}{}^{1}$, $EH_{8x}{}^{2}$ are the respective protonated forms:

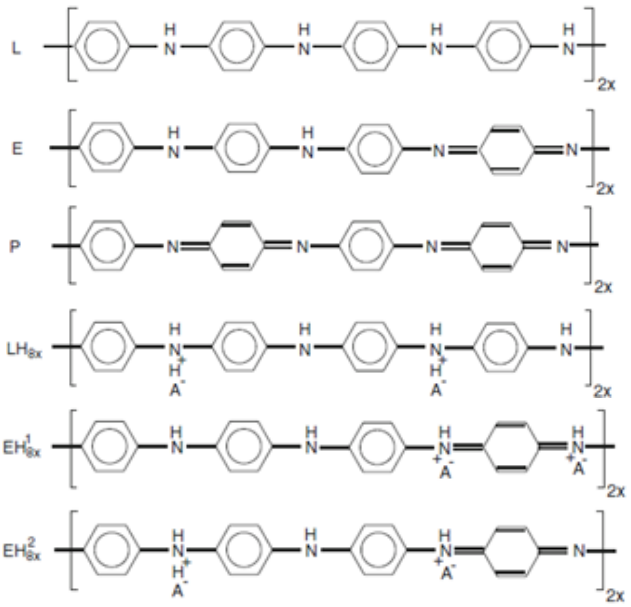
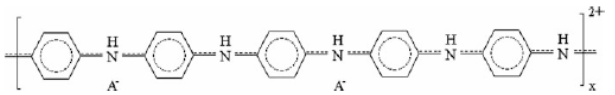


Illustration of delocalization (polaron lattice) of the emeraldine state:



[2]

Another application of these high surface area materials is to act as functional scaffolds for inorganic nanoparticles. The facile and reversible oxidation and reduction of polyaniline allows the polymer

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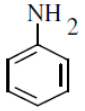
to behave as either an oxidizing agent or a reducing agent when combined with different materials. Treatment of polyaniline nanofibers with metal salts allows polyaniline to act as a reducing agent that donates electrons to the oxidized metal ion, causing deposition of metallic particles on top and within the polyaniline nanofiber network. The resulting inorganicorganic nanocomposite materials maintain the high surface area and dispersibility of the original polyaniline nanofibers and thus can be deposited and used as sensor materials or other electronically active materials. Gold-decorated polyaniline nanofibers have been explored for use in bistable memory devices.

Polyaniline nanofiber composites with metal nanoparticles can also be used in heterogeneous catalysis. Reduction of palladium (II) salts by polyaniline produces very small particles of palladium (0), the catalyst used for carbon-carbon bond formation between aromatic molecules in Suzuki coupling reactions. Since polyaniline nanofibers form a dispersion and not a solution, centrifugation can be used to pull the dense fibers out of the dispersion in order to recover the product of coupling reactions without timeconsuming extraction steps [1].

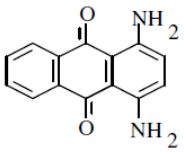
The technology has long been known for dyeing with aniline as an oxidizable dye, but the problem is to restrict the oxidation to the stage of emeraldine salt formation.

Aniline may be considered as an analog of dispersed aminoanthraquinone dyes, and correspondingly at the sorption stage one can use dyeing modes employed for ordinary dispersed dyes:

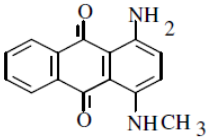
Aniline



Dispersed violet K



Dispersed violet 4C



A two-stage process can be used in dyeing fibers, for example, of polyamide, with the formation of an electrically conducting dye: polyaniline (sorption of the aniline by the fiber in the first stage as a dispersed dye and subsequent oxidation in the second stage), or in a single stage with parallel sorption and oxidation [3].

Materials and methods

Obtaining of core pigments. A sulfur alloy with calcium oxide was preliminarily prepared. For the production of alloys, the ground powders of sulfur and calcium oxide (2:3, 5:3, 1:10, 1:1) were placed in a porcelain crucible covered with a watch glass and heated to 115°C for 15 min. The resulting alloys were cooled and ground in a mortar. A sulfur alloy with calcium oxide in various molar ratios was added to a pre-prepared solution of aniline hydrochloride. Then, with constant stirring, a solution of ammonium persulfate ($n(C_6H_5NH_2)$: $n((NH_4)_2S_2O_8)$ = 1:1.25) was added. The reaction was carried out for two hours at room temperature and constant stirring. The precipitate was then filtered off, washed with three portions of 0.2M HCl and acetone and air dried.

Ratio of reagents:

a) aniline hydrochloride (0,005 moles, 0,648 g), ammonium persulfate (0,00625 moles, 1,425 g), sulfur (0,002 moles, 0,064 g), calcium oxide (0,003 moles, 0,168 g). The molar ratio is 1: 1,25 :0,4:0,6.

b) aniline hydrochloride (0,005 moles, 0,648 g), ammonium persulfate (0,00625 moles, 1,425 g), sulfur (0,005 moles, 0,16 g), calcium oxide (0,003 moles, 0,168 g). The molar ratio is 1:1,25:1:0,6.

c) aniline hydrochloride (0,01 moles, 1,295 g), ammonium persulfate (0,0125 moles, 2,85 g), sulfur (0,02 moles, 0,64 g), calcium oxide (0,1 moles, 5,6 g). The molar ratio is 1:1,25:2:10.

d) aniline hydrochloride (0,01 moles, 1,295 g), ammonium persulfate (0,0125 moles, 2,85 g), sulfur (0,1 moles, 3,2 g), calcium oxide (0,1 moles, 5,6 g). The molar ratio is 1:1,25:10:10.

e) aniline hydrochloride (0,005 moles, 0,648 g), ammonium persulfate (0,00625 moles, 1,425 g), sulfur (0,002 moles, 0,064 g), aluminum oxide (0,003 moles, 0,306 g). The molar ratio is 1: 1,25 :0,4:0,6.

f) aniline hydrochloride (0,005 moles, 0,648 g), ammonium persulfate (0,00625 moles, 1,425 g), sulfur (0,005 moles, 0,16 g), aluminum oxide (0,003 moles, 0,306 g). The molar ratio is 1:1,25:1:0,6.

g) aniline hydrochloride (0,01 moles, 1,295 g), ammonium persulfate (0,0125 moles, 2,85 g), sulfur (0,02 moles, 0,64 g), aluminum oxide (0,1 moles, 10,2 g). The molar ratio is 1:1,25:2:10.

l) aniline hydrochloride (0,01 moles, 1,295 g), ammonium persulfate (0,0125 moles, 2,85 g), sulfur (0,1 moles, 3,2 g), aluminum oxide (0,1 moles, 10,2 g). The molar ratio is 1:1,25:10:10.

Quantitative determination of sulfur in organic substance. A sample of the material is weighed, placed in a round-bottomed flask, 3 drops of 4% NaOH solution are added and 10 ml of 30% hydrogen peroxide is added. The flask is covered with a watch glass, heated to a boil and boiled for 20 min-

utes. Then add another 10 ml of 30% hydrogen peroxide and continue to boil for another 30 minutes. Then add 30-40 ml of distilled water and continue to boil until about half the content of the flask is reduced. The solution is then filtered. An excess of 0.1 M $BaCl_2$ solution was added to the filtered solution. A white precipitate is formed. It is filtered on a pleated filter, dried and weighed. The sulfur content in the material is calculated by the formula:

$$W(S) = m(BaSO_4) * 32{,}06*100/ 233{,}4 * m(sample);$$

sample weight is 0.1 g.

Results and discussion

When applying a layer of polyaniline to sulfur alloys with calcium oxide, color changes in powders were observed with a decrease in the molar content of PANI. Photographs of powders are given below.

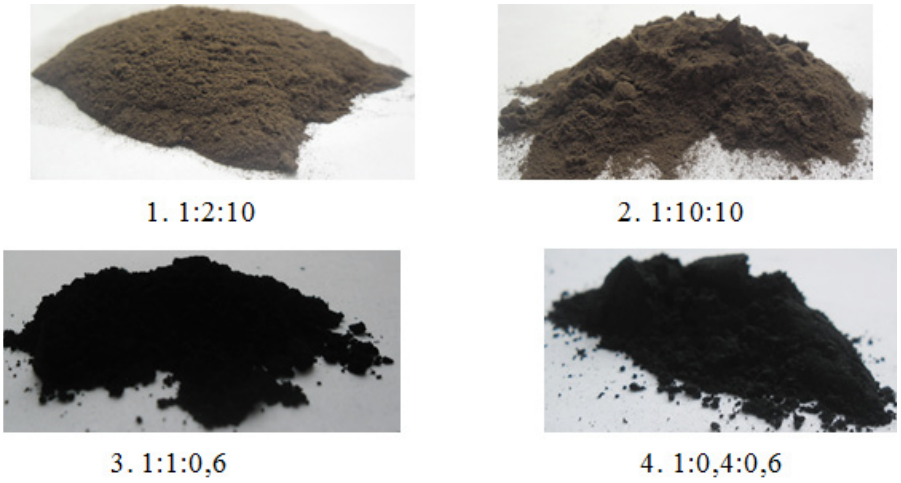


Figure 1 – PANI-S-CaO composites with different molar ratios

For the detection of by-products formed by the addition of sulfur alloys with calcium oxide, an analysis of the UV spectra of aqueous filtrates was carried out. On their basis, it can be said that when a calcium oxide is added to the composites, the hypochromic shift is noticeable.

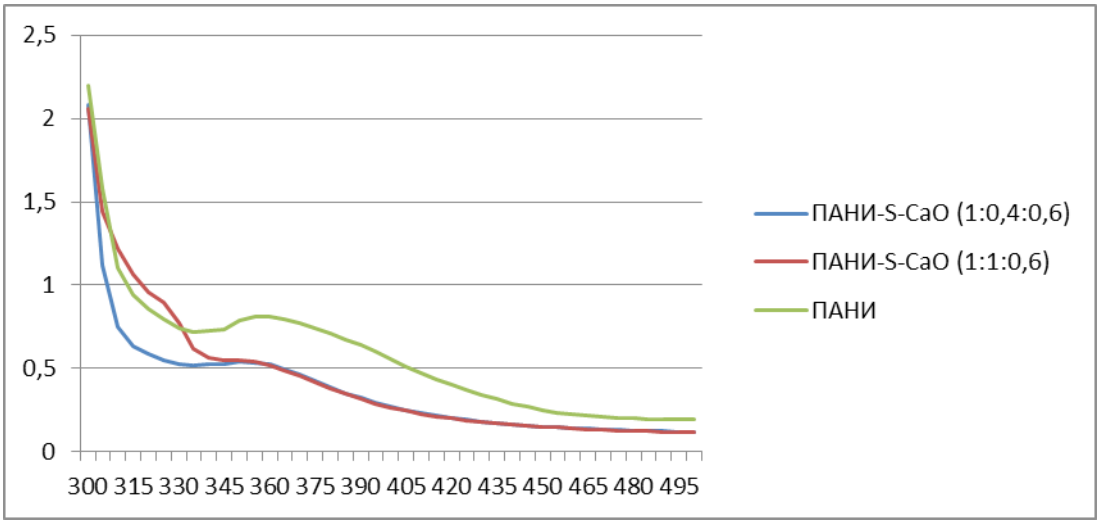


Figure 2 – UV spectra of PANI filtrate and PANI-S-CaO composites with different molar ratio

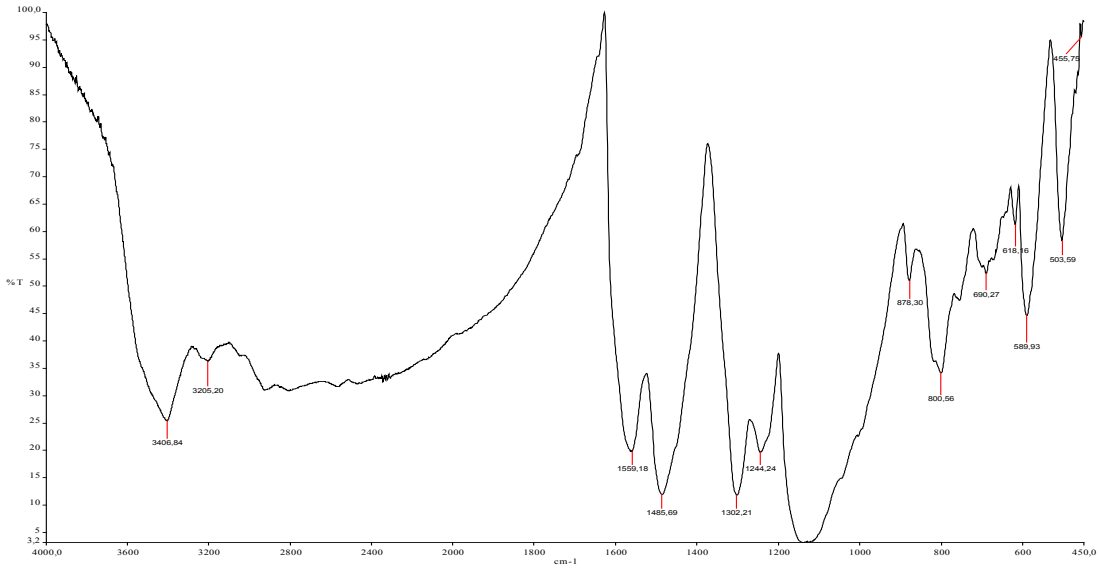


Figure 3 – IR spectrum of PANI-S-CaO composite (1: 1: 0.6)

Three peaks are observed in the PANI-S-CaO (1: 1: 0.6) spectrum, which are absent on the spectra of PANI and its composite with aluminum oxide: 3205, 618 and 456 cm^{-1}. The first of the peaks is characteristic of the bound -OH group in intracomplex compounds, the second for -C-S-, the third for -S- S-. What is said about the binding of sulfur with polyaniline. On the basis of this spectrum, it can be concluded that the organosulfur compound is formed.

After applying polyaniline to powders of sulfur-alumina alloys, the resulting composites had physical properties characteristic of PANI.

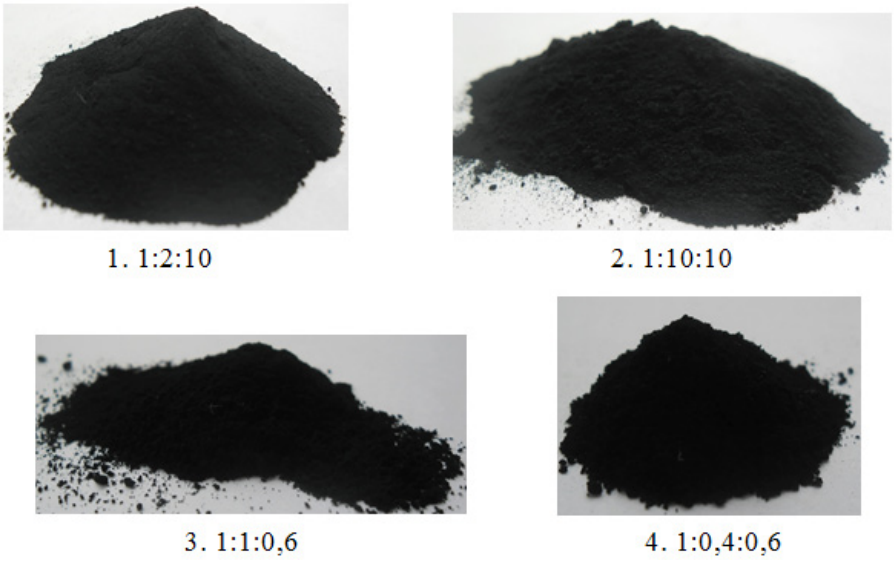


Figure 4 – PANI-S-Al_2O_3 composites with different molar ratios

To detect the by-products formed by the addition of sulfur alloys with alumina, an analysis of the UV spectra of aqueous filtrate was carried out. On their basis, it can be said that no side reactions are observed when alumina is added to the composites.

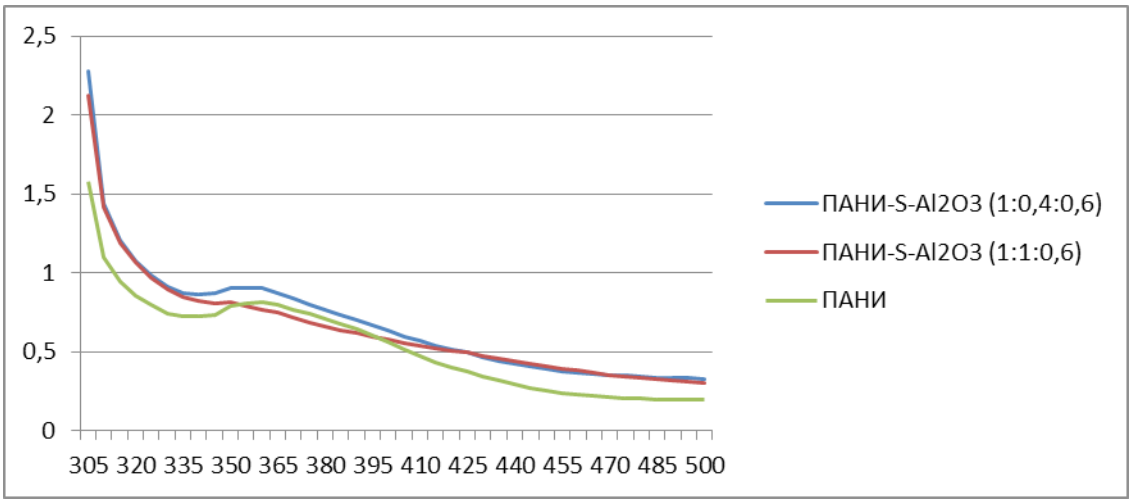


Figure 5 – UV spectra of PANI filtrate and PANI-S-Al_2O_3 composites with different molar ratio

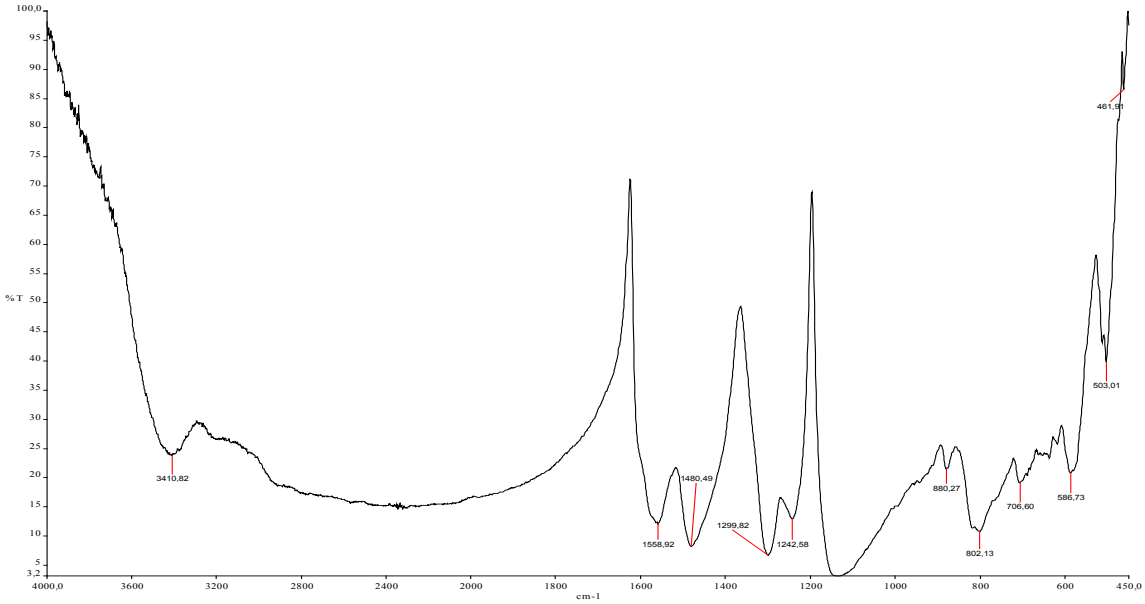


Figure 6 – IR spectrum of PANI-S-Al_2O_3 composite (1: 1: 0.6)

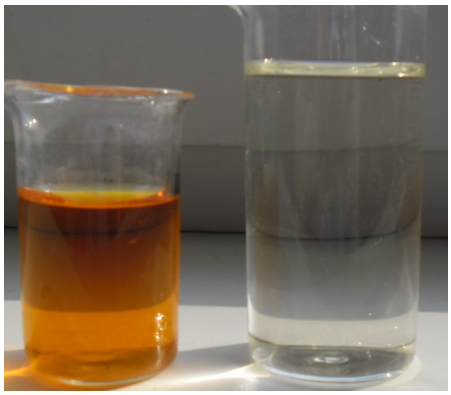


Figure 7 – Solution of methylorange before and after addition of adsorbent – PANI-S-Al_2O_3 composite (5: 2: 3)

The IR spectrum of the PANI-S-Al_2O_3 composite (1: 1: 0.6) is similar to the spectrum of polyaniline.

The property of polyaniline composites with oxides of various metals, such as the adsorption of dyes from wastewater, has been well studied. Thus, 8 mg of the composite adsorbs methylorange from a solution with a concentration of 0.06 g / l.

Conclusions

The possibility of obtaining composites based on the interaction of aniline with sulfur and ammonium persulfate for the production of pigments. Pigments of different qualitative composition with different component ratios were obtained. The dependence of the color change of the resulting composites on the quantitative composition was found.

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