

Synthesis and Characterization of Nanosized Copper(II)-Phthalocyanine Pigment (P BI 15:3) with the Modified Surface. I

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The research activity presented in this paper is intended to investigating of certain valuable nanosized blue pigment (P BI 15:3) prepared by 3-way synthesis (functionalization reactions) and conditionin(dispersing with or without encapsulation), namely obtaining stable aqueous dispersions of blue pigment with modified surface used in medium nonspecific for pigments. The techniques employed to characterize the structure and properties of blue pigment dispersions with functionalized particles compared to the original powder product were characterized by Fourier transform infrared spectroscopy FT-IR, thermogravimetric analysis (TGA), elemental analysis (EA) and particle size distribution (the distribution and average of particle diameter).In our finding the nano-dispersions obtained contain functionalized blue pigment particles with or without encapsulation in the form of liposomes with the average diameter below 200-300 nm, representing good results.

Keywords: copper (II)-phthalocyanines (PBI 15:3), functionalization, modified pigment, phisico chemical caracterization and morphostructural

Aqueous systems are increasingly used in many applications such as automotive and industrial coatings, paints, papers, inks, toners, adhesives, latexes, etc. as manufacturers face increased pressure to replace conventional solvent based systems. Such aqueous systems are known and generally contain a colorant material, such as a dye, which is soluble in the aqueous vehicle, such as water or a mixture of water and a water-soluble or water-miscible organic solvent.

Although dye-based compositions are readily utilized, dyes have several disadvantages when used in aqueous systems. For example, dyes, being water-soluble in a water/organic mixture, may dissolve and run when exposed to moisture or water. Dyes also exhibit poor light stability when exposed to visible or ultraviolet light.

Pigments are also known as colorants in aqueous compositions but have not received a wide degree of acceptance in aqueous systems, because of problems associated with the performance and reliability of the composition. The interest in recent years for nanostructured pigments with modified surface is justified by the extension of their use in application areas nonspecific for pigments due to their large sueface area, high rate of reactivity and due to the possibility of enhancing environmentally friendly reactions.

It is know that the organic pigments have exceptional physico-chemical and characteristics color demonstrated in textile printing, varnish and paint, but have many disadvantage related to their total insolubility in water or organic solvents and their crystalline form very hard which is extremely difficult to process for to be widely used.

Many researches and companies are concerned in recent decades working to find out pigments to extend the area of application. Thus, was found the method to prepare so-called *self-dispersible* pigments with improved properties and easier to apply.

Pigments known as *self-dispersible pigments* or *self-dispersing pigments* are created with the modification of their particles surface. Such pigments with surface modified can be obtained in a variety of ways including, but not limited to : oxidation(treatments with alkali salts of hypochlorite or ozone), or reaction with diazonium salts of aromatic amino acids or sulfonation or sulfonation + oxidation reactions.

Consequently, our team has applied all known synthesis pathways.

In order to control particle size and obtain dispersed nanoparticles with a narrow size distribution , various techniques of conditioning have been employed such as: dispersion (using shear forces) and encapsulating of the pigment functionalized, with lecithin to form liposomes.

These *pigments* with *modified surface* have the distinct advantage of being self-dispersible in aqueous media and can be used without a corresponding dispersing agent.

It is well known that the morphology and size of particles have a great impact on their chemical and physical properties.

The blue pigment nanoparticles with various structures, sizes, and morphologies were obtained and characterized.

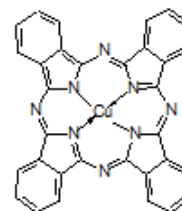
Experimental part

Materials

The chemicals used in our research were:

a) Pigment as powder: Copper (II)-phthalocyanine blue (PBI 15:3) (Colour Index No. 74160) - Hostaperm Blau B2G, purchased from CHIMTITAN SA , Bucuresti

Chemical structure (1)



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Molecular formula : $C_{32}H_{16}CuN_8$; CAS No.147-14-8 ;
Molecular weight: 575.5g/mol

Color: greenish blue

Synonyms: Pigment blue 15; Cu(II)phthalocyanine;
Cupru tetrabenzoporfir- azina; Tetrabenzo- 5, 10, 15, 20-
diazaporfirino-ftalocianina.

Copper (II)-phthalocyanines is a copper complex
[Cu(II)] of the compound tetra -aza- tetra-
benzoporphyrin.

b) Technical sulfuric acid

c) 4-aminobenzenesulfonic acid (Sulphanilic acid)

99.5% RPE-ACS, Analyticals Carlo Erba

d) Nitric acid 65 %

e) Technical hydrochloric acid (HCl)

e) Sodium nitrite 98 %

f) 4-Aminobenzoic acid, 99 %, Merck

g) Lecithin-paste, min 62% was selected as a
phospholipid; lecithin is a natural, non-toxic and
commercially available emulsifying agent.

Work equipment

Synthesis equipment (functionalization pigment)

Glass equipment for laboratory and micropilot

The micro/nanodispersion consisted in application of
shared forces to the compounds, stirring at 2000-12000
rot/min using: DRAIS lab-scale pearl mill (pearl $\varnothing = 3\text{mm}$)
and Homomixer UltraTurrax model T18 (IKA Works, USA),
and exposure to sonic vibrations in a lab-scale VCX 750 -
Ultrasonic Processor 750 W Sonics (Sonics & Materials,
Inc,CT-USA).

The encapsulation was made with the same dispersing
equipment

Experimental part

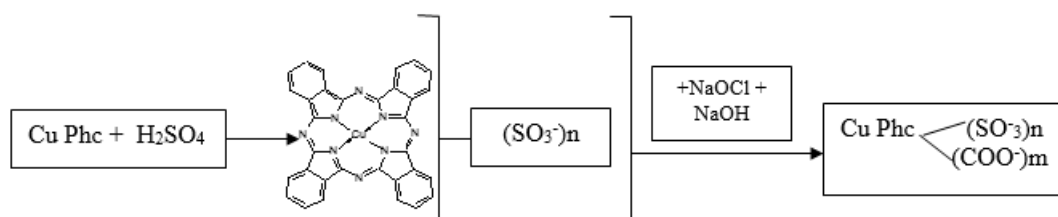
Working techniques

A- Functionalization by synthesis

B-Micro/nanodispersing

C-Micro/nanoencapsulation

A. Synthesis of modified pigment by functionalization



where:

Cu Phc is phthalocyanine blue pigment; $n=0.5-1$
sulfonic acid groups; $m=1-10$ carboxyl groups

The working method

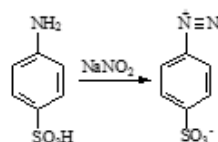
The commercial phthalocyanine blue pigment, powder
(Phc) were sulfonated with sulfuric acid 95% (the weight
ratio 1:5), at 120°C for 24 h. The reaction mixture was
cooled below 100°C and quenched in much water and
ice. The solid product was isolated by filtration and washed
with distilled water up to free of dissolved materials. Was
obtained the sulfonated phthalocyanine blue pigment (PhcS)
which is subjected to the oxidation reaction with
sodium hypochlorite in alkaline medium. The resulting
reaction mass is filtered and washed with distilled water
yielding the pigment functionalized (PhcSO) with the more
functional groups: SO_3^- si COO^- .

The cake was dispersed with specific equipments.

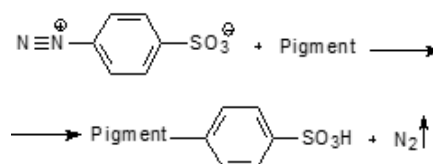
a. Attaching functional groups using diazotization
reaction of aromatic amino acids

The functionalization of the phthalocyanine blue
pigment (P Bl 15:3) was carried out by the reaction with
diazonium salt obtained by the reaction of para-
aminobenzenesulfonic acid (Sulfanilic acid) or para-
aminobenzoic acid with sodium nitrite in acid medium.

Diazotization of the sulfanilic acid or p-aminobenzene-
sulfonic.



The functionalization reaction of blue pigment particle
by sulfonation



The working method

Functionalization process included the following main
operations: dispersion of the pigment in the aqueous
dispersion of the aromatic amino acid, at 70°C under stirring
(6000 rot / min), followed by cooling of the reaction mass
at 0-5°C and introduction of an aqueous solution of 20%
sodium nitrite in acid aqueous medium; is adjusted pH to a
value 2, maintaining the reaction temperature at 0-5°C
under stirring for 1 h, then increase the temperature to
room temperature; filtering of functionalized pigment
obtained and the use further of functionalized pigment
(PhcD) in paste form or in dispersion form

b. Attaching functional groups using sulfonation and/or
oxidation reactions

Functionalization phthalocyanine blue pigment (P Bl
15:3) was carried out by the sulfonation reaction or
sulfonation + oxidation reactions [3].

B. Micro / nanodispersing operation

Dispersion is the term used to describe the finer grinding
and possible distribution of a substance in another, and the
resulting mixture is called dispersion.

A dispersion contains one or more phases dispersed in a
phase continua. Thus, in contrast to *the mixing*, the purpose
of dispersing operation is not to achieve a mutual
interpenetration of the individual phases, but to achieve
the finest *shredding* possible and uniform distribution of
one or more phases in a continuous phase.

The roles of the dispersing phase are:

-distributia uniform and reproducible of one or more
components in a continuous phase with a minimum energy
supply necessary;

- achievement of particles with defined sizes for the
disperse phase, the smallest particles corresponding to a
large contact area per unit volume between the disperse

and continuous phases and a narrow particle size distribution

There are two general types of dispersion devices: dynamic and static equipment.

In our research we used both types of devices.

The working method

At this stage PhcS or PhcSO were continuously mixed under high shear conditions for a sufficient amount of time to form a reaction product comprising a surface modified pigment *dispersed*. The mixing takes place in a suitable vessel under high shear conditions and utilizes equipment capable of providing a continued particle size reduction. A *high shear* means an energy sufficient to reduce the particle size distribution of the blue pigment functionalized to a desired size.

It has been used following equipments: Drais Ball Mill with 2000 rpm, Ultraturrax T18 with 6000-12000 rpm si Ultrasonic Processor 750 w with different times of dispersion.

C-Micro/nanoencapsulation

Encapsulation is a technique of packing, the operation of forming capsules having a core containing an active entity and a body of encapsulating surrounding that core. When the capsule is at micron size, the operation is called microencapsulation and when the operation is at nanometric level is called nanoencapsulation.

Enable central entity (core) of the capsules may be: solution, emulsion, dispersion, solid, etc., and the body (membrane) that surrounds the capsule can be made of different substances: starch, gelatin, sugars, dextrin, polymers, resins, etc. The capsules can be isolated as such or can be placed in an liquid external environment, thereby forming: micro / nanoemulsions, micro- / nanodispersion, liposomal formulations.

We chose micro/nanoencapsulation in liposomal formulations.

Liposomes are artificial vesicles, microscopic, wrapped in a lipid membrane and are well known for their medical uses. They are in the form of suspensions of spheroidal corpuscles, sized between 20nm and 10 micrometers.

The liposomes have the ability to incorporate ions, molecules, heavy metals and other materials, making it possible to use them in various fields indispensable modern human society.

One of the products frequently used in the preparation of liposomes is lecithin (L) from egg or soy, which is a natural emulsifier and is very accessible commercially.

The special quality of liposomes is that they give the possibility of using together in formulations, both soluble and insoluble materials, with or without using surfactants or other emulsifiers. Therefore the main advantage of liposomes is that they can hold together into a microsphere the materials that are normally immiscible, from which occurs controlled release of ingredients.

The microencapsulation technique for obtaining liposomes incorporating pigments is very new and little known. We headed attention on techniques for obtaining of micro/nanodispersions in liposomal formulations containing functionalized organic pigments (PhcS or PhcSO or PhcD).

The use lecithin from soy(Ls) as a material for encapsulation favors the penetration of colorant material inside the support for application.

The working method

The encapsulation operation preferably is prepared in the same equipment used in the high shear mixing step

where takes place dispersing operation. As encapsulation agent has been used the lecithin in aqueous medium at room temperature, in a weight ratio P/Ls is 1/0.5 up to 1/1

Physico-chemical and morphostructural characterization

To highlight the attachment of functional groups on the particle surface of a phthalocyaninic blue pigment by sulfonation (PhcS), sulfonation + oxidation (PhcSO) or (PhcD) diazotation of aromatic amino acids have been done spectroscopic, elemental, thermogravimetric and differential scanning calorimetry analysis.

Spectral analysis has been done by Fourier transform infrared spectroscopy, FTIR, in transmission mode.

FTIR spectra of phthalocyanine blue pigment standard, sulfonated phthalocyanine blue pigment (PhcS), sulfonated-oxidised phthalocyanine blue pigment (PhcSO) and phthalocyanine blue pigment (PhcD) were recorded on a Perkin Elmer GX spectrophotometer, with a resolution of 4 cm⁻¹, from 4000 cm⁻¹ to 400 cm⁻¹. Pellets were prepared by pressing a mixture of approximately 1 mg, from each type of pigment, and of approximately 200 mg of KBr (spectroscopy grade, Sigma-Aldrich).

Elemental analysis of all types of modified blue pigment has been done on a Perkin-Elmer 2400 Series II CHNS/O Analyser, at 975°C combustion temperature, at 500°C reduction temperature, upon 2-3 mg of pigment samples, in order to characterize the content (mass %) of carbon (C), hydrogen (H), nitrogen (N) and sulfur (S) in the samples.

Thermogravimetric analysis

The thermal stability of the self-dispersible pigment samples was investigated by thermogravimetric (TG) analysis at heating rate of 10°C min⁻¹ under a nitrogen atmosphere. The recorded TG curves and the differential TG (DTG) curves for selected pigments are presented in figure 5.

Size and particle size distribution of pigments functionalized compared to standard powder pigments

Equipment used. Determination of particle size has been achieved with the apparatus Zetasizer (Malvern ZetaSizer Nano ZS (Malvern Instruments, UK)

Technology integrated into the Zetasizer Nano ZS offers sensitivity and elasticity. Nibs existing optical system allows measurements of samples without dilution or with little dilution.

Particle size - the system enables measurements of particles from 0.6 nm to 6 microns.

Zeta potential - the system ensures accurate measurement of zeta potential in aqueous and non-aqueous dispersion.

Molecular weight - the system provides the sensitivity and stability required for absolute molecular weight measurement.

Zetasizer Nano ZS is able to analyze with accuracy, reliability and repeatability size. Nibs technology (noninvasive technology with retrograde laser light scattering) allows new levels of sensitivity in measuring particle size in the 0.6 nm to 6 microns.

Characterization of functionalized of phthalocyaninic blue pigment by sulfonation -Vis spectral characterization of pigments functionalized

The visible spectrum is domain of the length of electromagnetic waves which can be detected by the human eye. It consists of visible light waves with lengths

of approximately 380 nm (ultraviolet light) and 780 nm (infrared light). The visible spectrum is the part of the electromagnetic radiation and the human eye detects only this part of the field and the brain interprets them as colored light.

For spectral characterization of dispersions of pigments was used an M40 Specord spectrophotometru from Carl Zeiss Jena company equipped with device (support for cuve with small engine) in order to maintain the pigments in suspension (magnetic stirrer)

The samples subjected to measurements consisted of dispersions of pigments made and maintained in solution by diluting with distilled water and these samples were obtained before and after functionalization. The concentrations were in the range $2.5 \div 6.6 \times 10^{-3}\%$. The glass cuvette with layer thickness of 1 cm were used.

All samples analyzed were measured compared to a reference standard that has been distilled water.

Results and discussions

In accordance with the proposed objectives we synthesized functionalized phthalocyanine blue pigment in several versions and products were processed by dispersion and encapsulation in order to obtain new products that can be applied by dyeing on nonspecific surfaces (textiles, leather) .

To determine the performance of these products were made multiple characterizations physicochemical, morphostructural and coloristic.

Spectral analysis (fig 1, 2, 3, 4 are presented as Annexe 1,2,3,4)

It has been compared FTIR spectrum of phthalocyanine blue pigment as such, standard, with sulfonated phthalocyanine blue pigment FTIR spectrum (fig.1, 2, 3) and for both were identified characteristic copper

phthalocyanine absorption bands: -OH group at 3429 cm^{-1} , at 1625 cm^{-1} and at 623 cm^{-1} -CH₂ group at 2922 cm^{-1} and at 2852 cm^{-1} , C = C bound in aromatic ring at 1608 cm^{-1} , C=N group at 1505 cm^{-1} , C-C bound from isoindol at 1441 cm^{-1} and at 1330 cm^{-1} , C-N group from isoindol at 1288 cm^{-1} , C-N group at 1180 cm^{-1} and at 757 cm^{-1} , C-H group at 1118 cm^{-1} , 1091 cm^{-1} and at 1073 cm^{-1} , Cu ligand vibration at 904 cm^{-1} and at 878 cm^{-1} , C-H bound from aromatic ring at 1465 cm^{-1} , 755 cm^{-1} , 737 cm^{-1} and at 696 cm^{-1} , and C-C bound from aromatic ring at 664 cm^{-1} .

The -SO₃H group for sulfonated phthalocyanine blue pigment (PhcS) was identified at 1390 cm^{-1} and at 1027 cm^{-1} (fig.1, 2, 3)

The next step of the FTIR study was focused on characterization of sulfonate-oxidised phthalocyanine blue pigment (PhcSO). For this compound were identified characteristic absorption bands both for sulfonated and oxidized form such as: C = O group at 1767 cm^{-1} and at 1722 cm^{-1} , C = C group at 1667 cm^{-1} and at 1588 cm^{-1} , -OH group at 1640 cm^{-1} and at 631 cm^{-1} and -SO₃H group at 1392 cm^{-1} and at 1029 cm^{-1} (fig.1, 2, 3).

For modified phthalocyanine (PhcD) were identified diazo group, -N=N-, characteristic absorption bands at 2949 cm^{-1} , at 2817 cm^{-1} and at 1389 cm^{-1} , which means that the diazotization of the sample occurred (fig. 4).

Elemental analysis

Elemental analysis results of these compounds show good agreement with the theoretical values.

For PhcS the found values correspond to phthalocyanine blue pigment monosulfonated, but to a small extent. For PhcSO the found values for elemental analysis show that the oxidation process took place, but to a small extent. For PhcD the found values of elemental analysis show that the functionalization process took place.

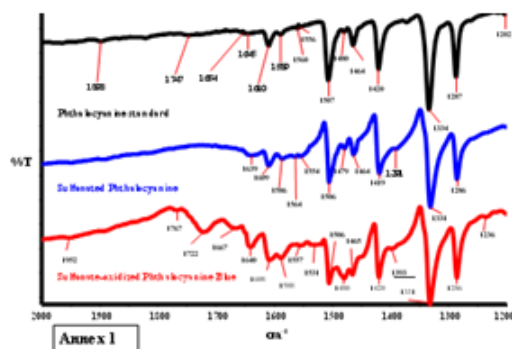


Fig.1 FTIR spectrum (2000-1200cm⁻¹) of PhcS + PhcSO

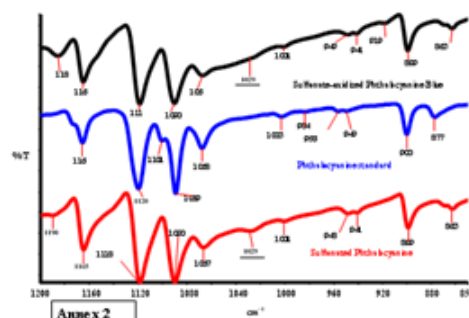


Fig.2 - FTIR spectrum (1200-800 cm⁻¹) of PhcS + PhcSO

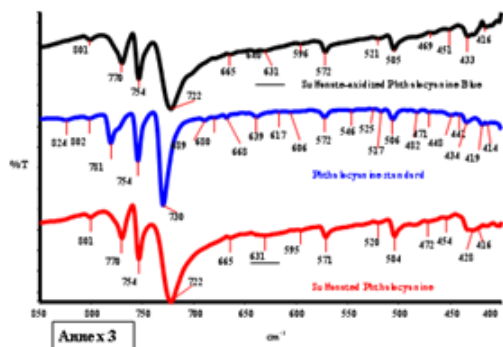


Fig.3 -FTIR spectrum (800-400 cm⁻¹) of PhcS+ PhcSO

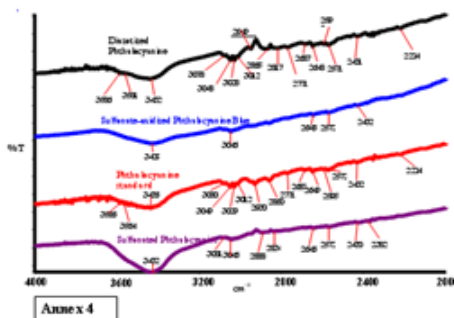


Fig.4 FTIR spectrum of PhcD

Table1
ELEMENTAL ANALYSIS

Sample	Carbon	Hydrogen	Nitrogen	Sulfur
Phthalocyanine blue pigment, standard (Phc)	68.63	3.09	18.95	-
Sulfonated phthalocyanine blue pigment(PhcS)	58.88	3.21	16.88	2.42
Sulfonate-oxidised phthalocyanine blue pigment(PhcSO)	52.26	2.73	14.80	0.97
Phthalocyanine blue pigment (type PhcD)	66.07	3.59	18.05	3.12

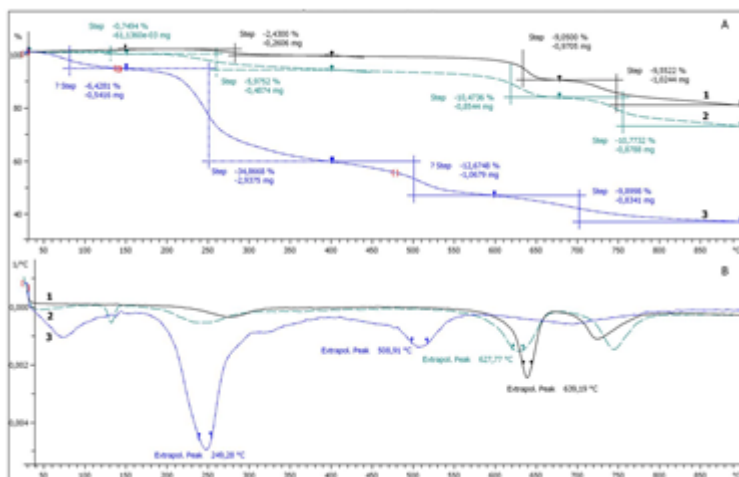


Fig. 5. TG (A) and DTG (B) curves of pigments: 1= phthalocyanine (Phc); 2= PhcD; 3= (PcS)

Thermogravimetric analysis

From figure 5, below 400°C, a small weight loss can be observed which means a good thermal stability of Phc. The second step of degradation at 400–680°C with T_{DTG} at 639.2°C, correspond to 9.1% can be assigned to the decomposition of Phc. The total weight loss by Pc was 21.1%. It is well known in literature that phthalocyanines and their metallo derivatives are stable up to 400 °C [1].

Four weight loss stages are observed in the thermogram of sulfonated phthalocyanine (PhcS-3) and PhcD (2). The weight loss at up to 400 °C can be attributed to desorption of water and decomposition of organic species, respectively. However, the weight loss starting at about 400 °C for PhcS (3) with T_{DTG} at 508.9 °C, correspond to 12.7 % and for PhcD (2) with T_{DTG} at 627.8 °C, correspond to 10.5% can be assigned to the decomposition of Phc. The total weight loss of PhcS was 63.9 % and of PhcD was 28.0 % from its initial value (fig. 5). These observations may indicate higher stability for PhcD, self-dispersible pigment samples.

DLS analysis

Average particle sizes in nm of functionalized phthalocyanine blue pigment compared to standards are presented in figure 6 and table 2.

It is found greater efficiency in the operation of dispersion and encapsulation for product.

PhcD compared to PhcSO but both are included on the range 150-300nm representing good results.

The coloristical characterize of the functionalized pigments -Vis spectral characterization

After the registration of absorption spectra of microdispersiilor obtained from pigments as such and functionalized resulted following:

- Absorption spectra of dispersions show that there was a functionalization process.

-The effect after the functionalization and the dispersing of blue pigment is shown by the fact that a part of it went into solution resulting in an increase of absorption and in some cases extending to a change in color (absorption maxima occur).

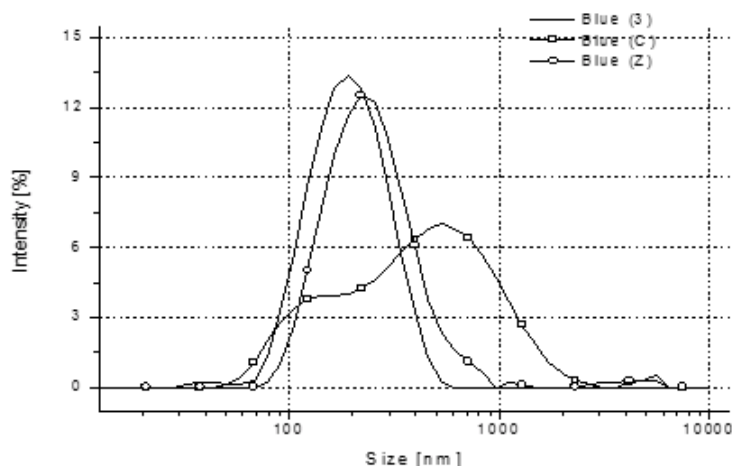


Fig 6. Particle size distribution diagram of functionalized phthalocyanine blue pigment (table 2)

	Cu-Phthalocyanine blue pigment
Standard powder (Hostaperm Blau B2G)	Z
<i>Diameter.(nm)</i>	238
Pigment functionalized by sulfonation + oxidation (PhcSO)	C -micro/nanodispersed
<i>Diameter.(nm)</i>	282
Pigment functionalized (diazotation)- (PhcD)	3 -micro/nanodispersed + micro/nanoencapsulated
<i>Diameter(nm)</i>	175

Table 2
AVERAGE VALUES (nm) OF
PHTHALOCYANINE BLUE
PIGMENT (PhcSO AND PhcD)

Sample indicative	Concentration in pigment (%)	Concentration recording ($\times 10^3$)	Maximum absorption (nm)	Absorption	Absorption coefficient
Standard	100	6.56	650...655	0.061	9.29
h	21.25 (p)	6.55	625	1.589	242.59

Table3
VIS SPECTRAL
CHARACTERIZATION

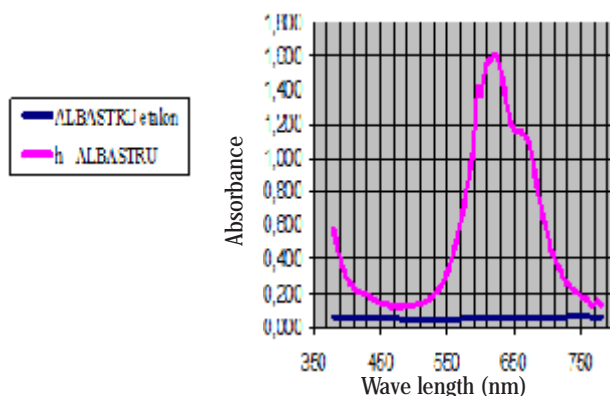


Fig 7. Absorption spectrum for blue pigment (P BI 15: 3) functionalized by sulfonation compared with the pigment as such

-Following functionalization there is a color enhancement of *solutions*. This can be seen from the increasing value of the absorption coefficient of the pigment functionalized to the reference value.

-Intensifying of color does not automatically mean an increase in coloring power in the sense that the substance may be colorful but not dye.

Conclusions

The phthalocyanine blue pigment functionalized by attaching chemical groups SO_3^- and COO^- was synthesized by methods described in the literature [2, 3, 5, 11]. So are obtained *self-dispersing pigment* means a pigment having stabilizing groups covalently attached to its surface such that the pigment forms a stable aqueous dispersion in the absence of any additional dispersing agent.

The structure of synthesized compounds respectively the phthalocyanine blue pigment functionalized/ modified (PhcS, PhcSO and PhcD) was proved by spectro-photometric analysis. In these spectra FT-IR is determined the existence mainly functional groups SO_3^- and COO^- confirming that the functionalization reactions occurred in given conditions. FT-IR spectral analysis finds that besides functional groups mentioned above the blue pigment functionalized also contains a lactone group, a phenolic group, a quinone group and combinations thereof attached to the surface of the pigment.

By Vis spectral characterization, the absorption spectra of nanodispersions show that there was a functionalization process. Following functionalization there is a color enhancement of *dispersions*. This can be seen from the increasing value of the absorption coefficient of the pigment functionalized to the reference value.

The functionalization reactions bring greater load density of hydrophilic groups around of the particle forming so-called *self-dispersible* pigments.

The functionalised phthalocyanine blue pigments were dispersed in an aqueous medium affording nano-dispersions confirmed by DLS analysis. We achieved such nanodispersions containing particles of 150-300nm with a cast majority in this area.

The dispersing operation of phthalocyanine blue pigments functionalized (PhcS; PhcSO; PhcD) continued with the encapsulation operation of functionalized blue pigment with lecithin favors deep dyeing on porous material in aqueous media (leather, textile).

In conclusion, this study demonstrated that obtaining the nanodispersion in the form of liposomal dispersions

may be beneficial to extend the scope of application of functionalized phthalocyaninic blue pigment in non-specific fields (ex. exhaustive dyeing in an aqueous medium).

List of abbreviations

Phc- Cu-Phthalocyanine blue pigment

PhcS- Sulfonated modified phthalocyanine blue pigment

PhcSO-Sulfonated carboxy modified phthalocyanine blue pigment

PhcD- Phthalocyanine blue pigment modified based on the diazotization reaction of an aromatic amino acid

Is- Lecithin from soy

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