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Purification and characterization of phthalocyanines

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The technical details of a simple train sublimation (carrier gas) system for purification of organic materials are given and the refining procedure is described. A study of the effects of purification on metal free phthalocyanine (H_2Pc), magnesium phthalocyanine (MgPc), copper phthalocyanine (CuPc), vanadyl phthalocyanine (VOPc), zinc phthalocyanine (ZnPc) and lead phthalocyanine (PbPc) was carried out by means of optical absorption, X-ray diffraction, electron paramagnetic resonance, sublimation behaviour and photovoltaic data. It was found that train sublimation improves the quality of the pigments considerably. Spectroscopic results indicate the presence of a second phase in the purified MgPc.

1. Introduction

In recent years organic materials have been recognized as a possible alternative to inorganic semiconductors in photovoltaic solar cell applications and much work has been done to study their photophysical properties. In our laboratory considerable effort was directed towards the development of Schottky-barrier photovoltaic cells employing a dispersion of phthalocyanine particles in a polymer binder as photoactive layer [1]. In spite of the progress made, it was recognized that the high internal resistance of this type of device imposes severe limitations on the photovoltaic output.

There are several possibilities to reduce the internal resistance of organic solar cells. One way is to reduce the thickness of the photoactive layer. For instance changing from a particle dispersion to ultra thin evaporated organic p- and n-type films. Tang *et al.* have shown earlier [2] that this is a feasible approach.

Further improvement of solar cell performance ought to be possible by means of doping and spectral sensitization. One of the objectives of our work is to examine the application of organic semiconductors in the fabrication of thin film p–n junction devices.

Metallophthalocyanines were chosen as p-type materials for this purpose because they possess well known photophysical properties and are thermally and chemically stable. But soon it became apparent that some of the phthalocyanine dyes, as obtained from the supplier, contained large amounts of unwanted impurities. This made sublimation very difficult, resulted in contamination of the vacuum system, and led to poor phthalocyanine films. If better results were to be obtained the dyes had to be purified prior to the vacuum sublimation. The purification method had to be fast, simple and inexpensive, which excluded the application of high vacuum sublimation techniques used by other workers [e.g. 3–5]. Instead the train sublimation approach was chosen.

The sublimation system set up for this work is described in some detail in the next section. The effect of purification on the physical properties of metal free phthalocyanine (H_2Pc), lead phthalocyanine (PbPc), copper phthalocyanine (CuPc), magnesium phthalocyanine (MgPc), zinc phthalocyanine (ZnPc) and vanadyl phthalocyanine (VOPc) was studied. The purified materials were characterized by several methods which are outlined in Section 3 together with the measured data.

The discussion of the results with the conclusions are presented in Section 4, followed by a summary of the purification study.

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2. Purification of phthalocyanines

The purification technique used in this work is known as train sublimation, carrier gas sublimation, entrainer sublimation or zone refining. (This type of zone refining should not be confused with the zone refining technique used in single crystal purification as for example described in [6].)

In spite of the fact that this method is referred to rather often in the literature [eg. 3, 7, 8] it is practically impossible to find exact technical details. Some parameters regarding the operation of a train sublimation are given in [9] and [10].

In order to correct this situation the apparatus and the purification process are described below in some detail.

2.1. The train sublimation system

Fig. 1 shows schematically the arrangement of the system components. The main element is a 500 mm long heater tube made from Cu, with an outer diameter of 50 mm and a 30 mm bore. The end where the sublimation takes place is heated by means of two heater bands, while the opposite end is cooled with a water coil ($\frac{1}{4}''$ Cu-tubing, 9 windings). Five small holes distributed evenly along the heater tube permit to measure the temperature profile with a thermocouple. The heater tube arrangement is mounted in an asbestos housing and thermally insulated with glasswool.

The material to be purified is placed into a glass tube, which is approximately 600 mm long and has a diameter of 25 mm. Pyrex glass is sufficient if phthalocyanines are purified (sublimation temperature 400 to 500° C), because this type of glass has a softening temperature above 580° C. The pyrex tube is inserted into the heater tube just so far that the dye is located between the heater bands (Fig. 2b and c).

A rotary vane pump is used to maintain a flow of purified N_2-gas through the system: this improves the heat flow in the glass tube and helps to transport the sublimed vapour towards the cooler end. An Edwards Pirani gauge indicates the gas pressure, whereas the flow rate is monitored with a Gilmont flowmeter No. Fl 200.

The liquid nitrogen cold trap prevents the contamination of the rotary pump by volatile impurities and decomposition products, which are released during the purification process.

2.2. Operation of the purification system

A good separation of purified materials and non-volatile impurities in the pyrex tube is obtained with a constant temperature gradient along the heated tube, i.e. when the temperature drops linearly with distance from the heater bands. Fig. 2a shows a typical temperature profile as observed during the purification of ZnPc. Such a

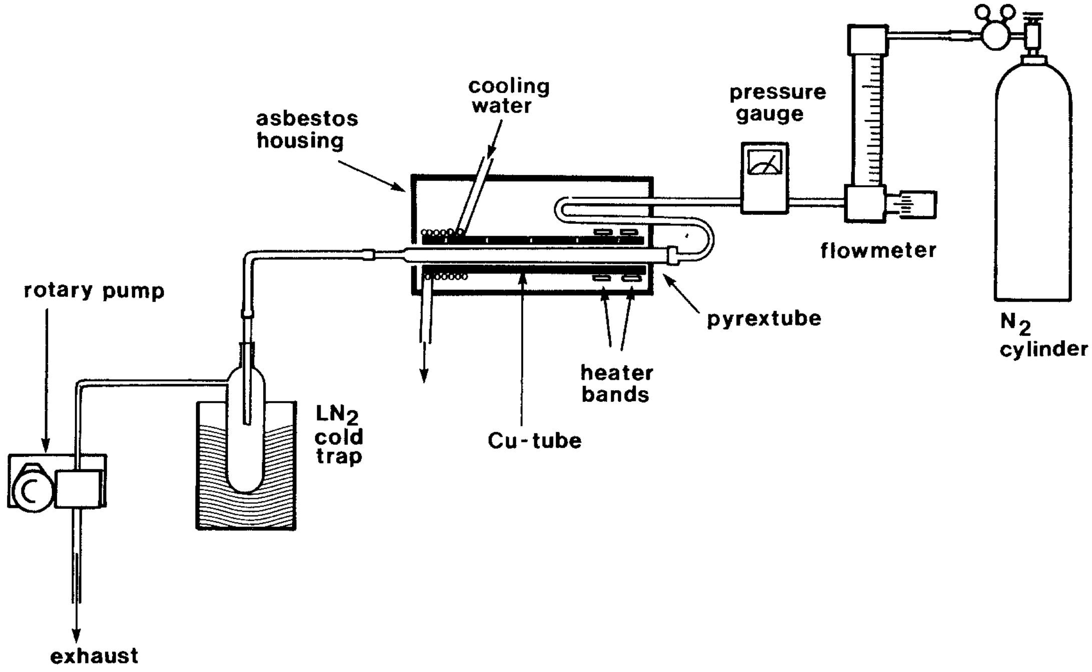

Figure 1 The train sublimation system (schematic).

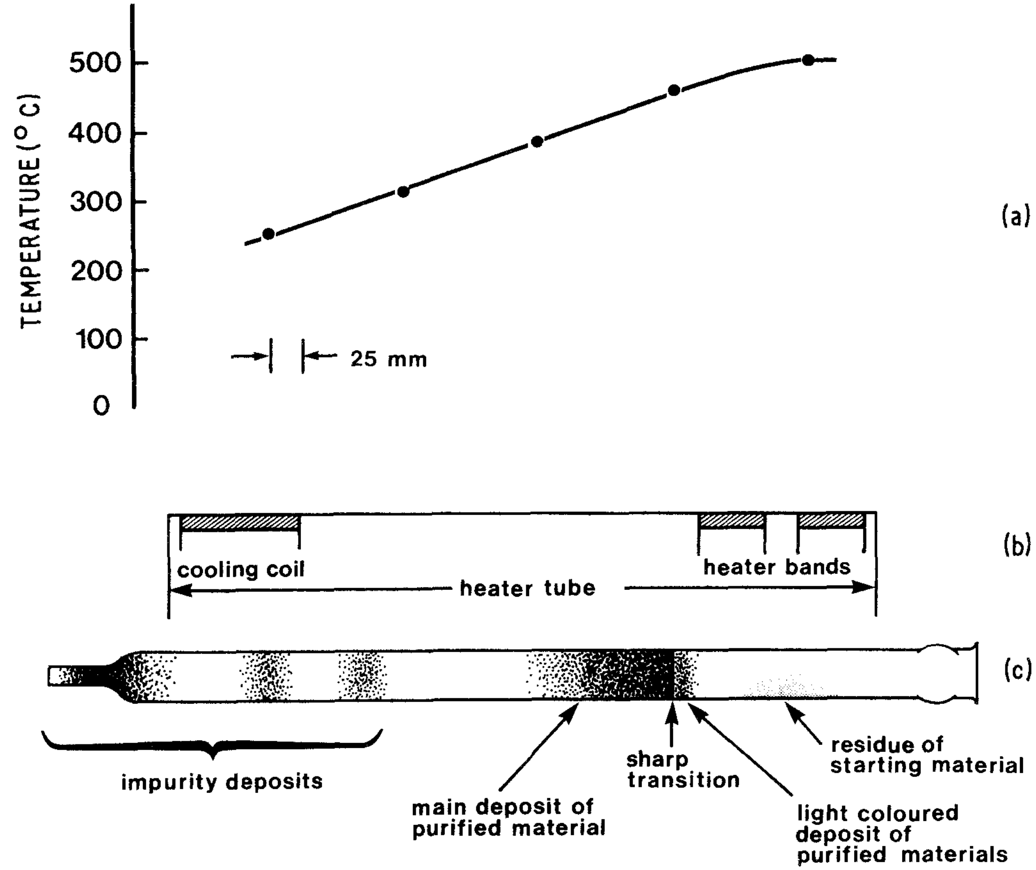

Figure 2 (a) Temperature distribution along the heater tube (typical); (b) relative positions of the system components, and (c) typical result of a train sublimation (ZnPc, heater voltages $U_1 = 136$ V, $U_2 = 102$ V).

linear temperature profile is achieved under the following conditions:

(a) the spacing between the heater bands is 25 mm;

(b) the voltage V_2 applied to the heater band towards the cold end is 25% lower than V_1 at the first heater band or $V_2/V_1 = 0.75$;

(c) the gas pressure is approximately 200 Pa;

(d) the gas flow-rate is approximately 1 l sec^{-1} at 200 Pa; corresponding to 14 l h^{-1} at atmospheric pressure.

Each purification cycle generates a Cu-oxide layer on the heater tube surface, which leads to a change in heat transfer from the heaterbands to the pyrex tube. Therefore it is not possible to give an absolute expression for the temperature as a function of the voltages applied to the heater-bands.

Under the conditions pointed out, it takes $2\frac{1}{2}$ to 3 hours for the system to reach maximum temperature and about the same time to cool down to 300 K once the heaters have been switched off. The pyrex tube is then taken out of the heater tube and cut into convenient sections. From these the purified material is collected and kept in tinted bottles to prevent ultraviolet exposure.

2.3. Sublimation results

Once the train sublimation process was completed at least five zones in the pyrex tube could be identified. A black fluffy low density powder remained, where the starting material had been. Only the H_2Pc (we used the x-form [11] as starting material) did not show this kind of residue; instead a trace of greyish-brown powder was left behind, which was retained for electron paramagnetic resonance (EPR) investigation. The black residues did not dissolve in hot α-chloronaphthalene or concentrated sulphuric acid, which indicated the absence of the starting material. All purified phthalocyanines formed two zones of deposits (Fig. 2c): a short ring of amorphous material with a lighter colour than the starting material, and a longer region of crystalline material which was darker in colour. The lighter deposits grew always towards the hot end and the transition between the two regions was abrupt with no space in between. Generally, the temperature at the transition line was 10% below the maximum temperature.

Following the purified phthalocyanine regions, several sharp zones of coloured impurities existed. The amount of impurity deposits at the cooled end (yellowish brown materials) demonstrated the variation in the purity of the starting materials. The purity of the phthalocyanine strongly depended on the supplier and varied from batch to batch. Materials which we have synthesized were relatively clean and only light brownish films formed as impurity depositions. Impurities from Eastman Chemical MgPc A7G and ZnPc produced brownish and white crystalline layers, which were approximately 2 mm thick. In case of Pfaltz and Bauer PbPc and Eastman MgPc A7J the impurity depositions blocked the exit of the pyrex tube when the same amount of starting material was used as with the other phthalocyanines.

The yield, i.e the amount of purified material collected from the pyrex tube with respect to the amount of starting material used also varied greatly with the degree of starting material purity. It was about 80% in case of VOPc, 42% for MgPc A7G and as low as 25% for PbPc.

No attempts were made to identify the impurities still present in the purified materials or to determine the nature of the impurity depositions in the tubes.

3. Characterization of purified phthalocyanines

To determine the effects of zone refining on the physical properties of phthalocyanines the purified materials were characterized by means of optical absorption, X-ray diffraction, EPR, photosensitivity, and vacuum sublimation behaviour.

Unfortunately, only little of the light coloured materials was deposited per purification, barely enough to prepare the samples for the absorption measurements. Therefore, none of the other characterization studies could be carried out on this type of purified phthalocyanines.

3.1. Optical absorption spectra

Absorption spectra of particle dispersions in polymer binder, prepared from the purified materials, have been measured, using the differential technique described in [9]. The light coloured materials and the darker species showed always the same spectra. Fig. 3 demonstrates this for PbPc.

The absorption characteristic of light blue H_2Pc (Fig. 4a) clearly identifies the β-polymorph [9]. The light coloured variety of ZnPc and CuPc exhibited similar spectra, i.e. they also deposited in the β-form. VOPc (Fig. 4b) shows a mixture of phase I and phase II polymorphs, according to the results given in [9].

In the case of MgPc (Fig. 4c), however, the absorption spectra not only showed the "normal" structures at 640 mm and 690 mm [12] but also an additional strong line at 850 nm, which to our knowledge has not been reported before.

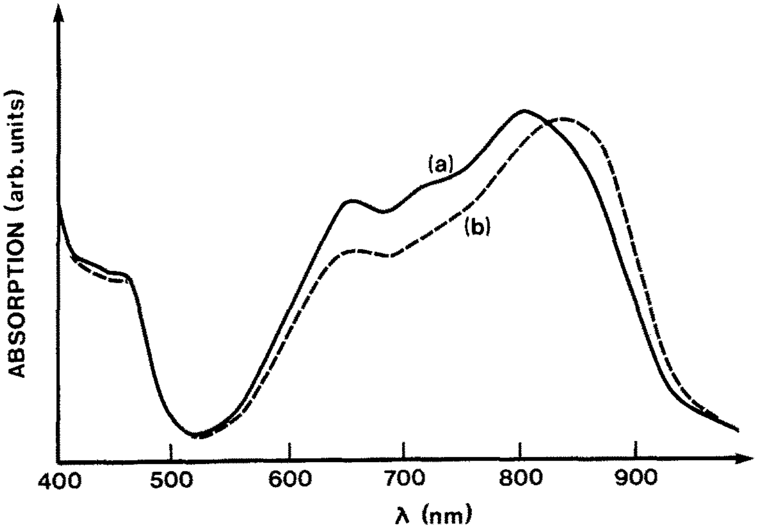

Figure 3 Absorption spectra of purified PbPc, (a) light coloured modification and (b) dark coloured modification.

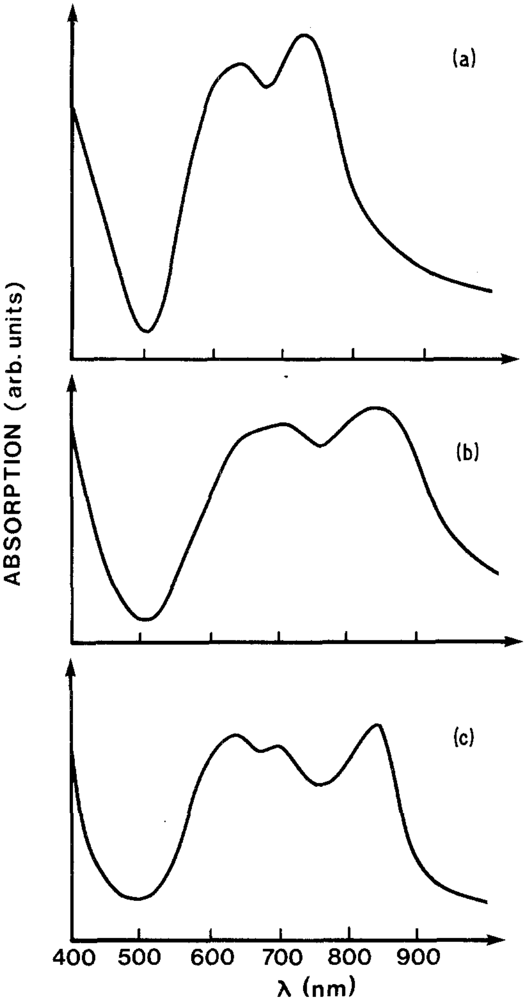

Figure 4 Absorption spectra of purified phthalocyanines (a) H_2Pc, (b) VOPc and (c) MgPc.

3.2. X-ray diffraction

The purified phthalocyanines were investigated by means of X-ray diffraction in order to establish their crystal structures. The results generally confirm the optical absorption data. Four phthalocyanines, namely H_2Pc, CuPc, MgPc and ZnPc, formed β-type crystallites. VOPc crystals were identified as phase II, whereas in the case of PbPc none of the known phthalocyanine structures could be identified. The data indicate a triclinic unit cell with the following dimensions, $a = 1.408$ nm, $b = 0.731$ nm, $c = 1.292$ nm and $\alpha = 96.1°$.

3.3. EPR-spectra

The EPR measurements were performed at room temperature using a Varian E102 spectrometer. Table I lists some of the measured results.

PbPc is known as a diamagnetic material [10], and should at best exhibit only a weak EPR absorption line. The observed strong signal of the unpurified material (Fig. 5a, α) must therefore originate in the admixed impurities. This line at $g \approx 2.003$, which is caused by free spins [8, 13], was considerably reduced in the purified PbPc (Fig. 5a, β), indicating the removal of a large part of the impurities during the purification process. The asymmetric shape of the EPR signal is typical for some diamagnetic phthalocyanines [13].

ZnPc also showed a strong reduction of the ESR spin signal after purification (Fig. 5b). This time the symmetric line shape is not changed.

The difference in signal characteristic was very pronounced in the case of CuPc (Fig. 5c). It changed from a powder type spectrum to one with more crystalline features, which makes it impossible to determine whether impurities were removed or not.

More complex spectra were obtained from the VOPc samples. Here the EPR signals (Fig. 5d) were a superposition of a broad single line and the unresolved octet of the VO ion [14]. The overall signal amplitude showed an increase of approximately 30% after purification.

x-H_2Pc showed the expected EPR spectrum [15]: a broad background signal plus the free spin line at $g \approx 2.003$ which is accompanied by the two nine line Cu-multiplets (Fig. 6). The amplitude ratio of free spin line to the strongest multiplet line was approximately $R = 2$. The transition from x to β form might account for the different background signal of the purified H_2Pc (Fig. 7). The free spin line and the multiplets were more dominant and R increased to ≈ 3. A comparison of the intensity of the free spin signal before and after purification gives an eightfold increase in the spin density (number of spins per mg).

The EPR spectrum of the H_2Pc residue shows the same general features as that of H_2Pc. The amplitude ratio, R, however, was 15 times higher ($R \approx 30$) and the free spin density was a factor of 46 higher.

In case of MgPc two batches were studied and therefore four samples are listed in Table I. MgPc2 was purified from batch A7G and MgPc10 from A7J under similar conditions. The EPR spectra resembled the inset of Fig. 7, i.e. they showed a strong free spin line at $g = 2.003$ and two Cu-multiplets sitting on a broader undergroud. The ratio, R varied from 200 to 400.

The two crude materials differed by $\approx 20\%$ in

TABLE I Results of EPR measurements

Sample	Free spin line*			Background line			Remarks
	Line width (G)	δ†	R‡	Line width (G)	δ†	g	
PbPc L02080	7.4	–	–	–	–	–	
PbPc purified	7.75	4.8×10^{-3}	–	–	–	–	
ZnPc A3B	5.63	–	–	–	–	–	
ZnPc purified	4.63	9.3×10^{-2}	–	–	–	–	
CuPc	–	–	–	–	–	2.076	line distorted, no free spin line observed
CuPc purified	–	–	–	45	–	2.067	
VOPc A§	–	–	–	381	–	2.018	
VOPc purified§	–	–	–	412	1.2	2.014	shows two weak lines at $g = 3.502$ and $g = 1.410$
x-H_2Pc	5.5	–	2	1175	–	2.035	
H_2Pc	6.25	8	3				background has complicated structure
H_2Pc residue	4.9	46	30	1350	–	2.505	
MgPc A7G	3.75	–	340	250	–	~2.003	
MgPc 2	3.75	1.8	400	250	–	~2.003	background lines dominated by multiplets
MgPc A7J	3.75	–	300	250	–	~2.003	
MgPc 10	5.1	1.7	200	250	–	~2.003	

*$g \approx 2.003$.

†$\delta = \dfrac{\text{spin concentration of purified sample}}{\text{spin concentration of crude material}}$.

‡$R = \dfrac{\text{amplitude of free spin line}}{\text{maximum amplitude of multiplets}}$.

§the free spin line might be hidden under the broad signal at $g \approx 2.016$.

spin concentration. This was not greatly changed by the purification, because both purified samples showed roughly the same increase $\delta \approx 175\%$ of the free spin density. It was found that δ increased in a linear fashion with the temperature, T, at which the train sublimation was carried out.

3.4. Effect of purification on the photosensitivity of phthalocyanines

In order to study the effect of purification on the photoelectrical properties of the phthalocyanines, Schottky type solar cells were prepared as described in [16]. From photovoltaic measurements the short-circuit currents and the charge carrier generation efficiency were determined (see Table II).

Cells 1 and 2 were made from unpurified and purified VOPc A respectively. For reasons which are not yet understood it was impossible to reduce the particle size of the purified VOPc to less than 2 μm, even after extended periods (16 days) of ball milling in methylene chloride [17]. Therefore, some of the purified material was further subjected to a single acid pasting process and then used to make Cell 3.

Cells 4 and 5 were prepared from untreated VOPc B and VOPc C respectively, two materials that showed high photosensitivity [18]. The results obtained for these two cells are included here to provide a "calibration standard".

From the data in Table II it is evident that the purification resulted in a 100% increase of photosensitivity (Cells 1 and 2). A reduction of particle size lead to another 50% increase (Cells 2 and 3) which amounts in a total sensitivity improvement of 300% (Cells 1 and 3). (The final stage of manu-

TABLE II Effect of purification on the photosensitivity of VOPc

Cell	Short circuit current J_{sc} ($\mu A/cm^2$)	Charge carrier generation efficiency at 620 nm, ϕ (%)	Materials used
1	21.0	8	VOPc A
2	45.5	17	VOPc A purified
3	65.0	25	VOPc A purified and acid pasted
4	76.0	29	VOPc B
5	96.0	37	VOPc C

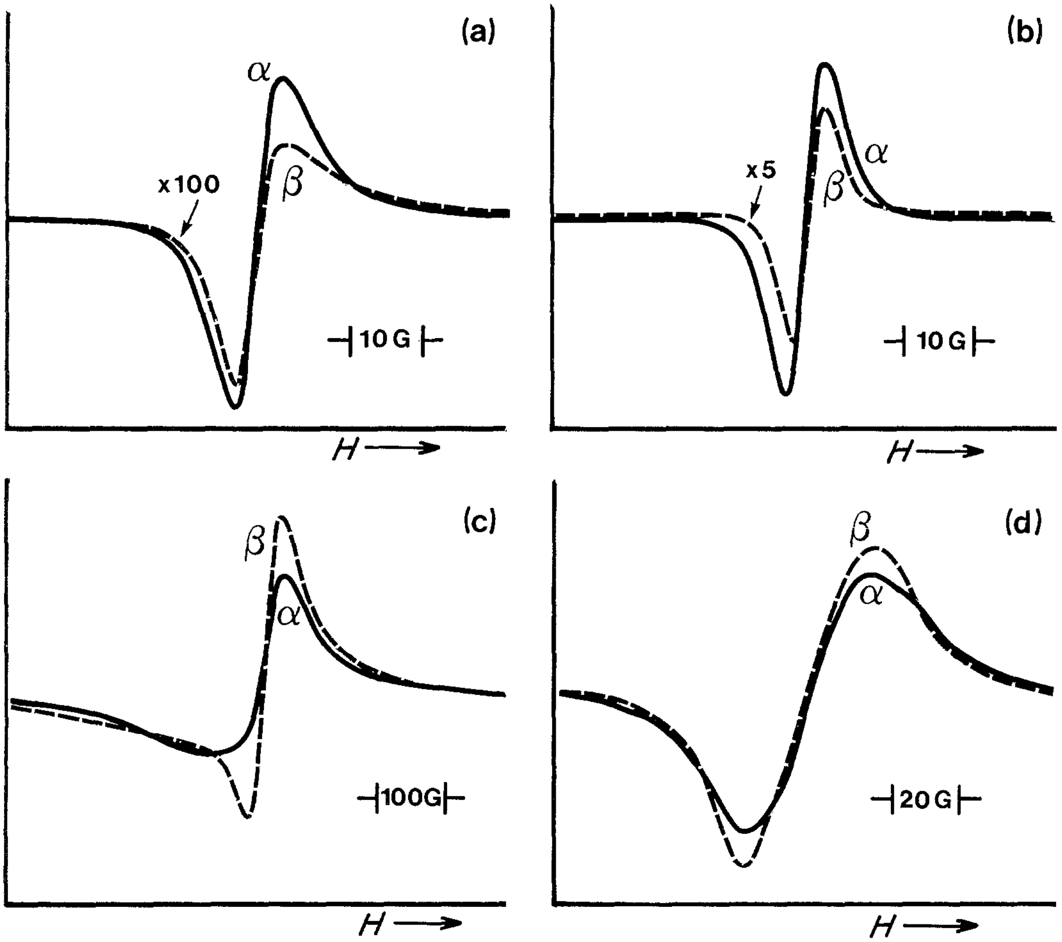

Figure 5 EPR spectra of unpurified (α) and purified (β) phthalocyanines (a) PbPc, (b) ZnPc, (c) CuPc and (d) VOPc.

facturing VOPc A comprised three acid pasting processes already. Therefore, the increase in photosensitivity from Cell 2 to Cell 3 cannot be caused by further purification during the additional pasting. Hence, it has to originate in the reduction of particle size which also occurs during this process.)

Comparison with Cells 4 and 5 furthermore indicates that the train sublimation of a relative poor material such as VOPc A [16] yields a purified product, with properties comparable to those of the best VOPc materials.

3.5. Vacuum sublimation behaviour

The change in behaviour during vacuum sublimation of films due to the purification was most drastic in case of MgPc, ZnPc, and PbPc (see Table III for MgPc). These materials needed an outgassing period of at least 1 h, when heated the first time, and still 20 to 30 min after several heating cycles. During the vacuum sublimations the pressure usually rose to more than 3.3×10^{-3} Pa. The onset of sublimation was not well defined and occurred over a relatively large range of the heating current. Also the rate of sublimation fluctuated strongly and puffing occurred rather frequently, i.e. unsublimed phthalocyanine powder was blown out of the boat onto the substrate, rendering the sublimed film useless. Once all the phthalocyanine was sublimed the same type of fluffy black residue remained in the boat, as was created during the train sublimation.

The other unpurified materials behaved not as badly. They needed less time for outgassing and sublimed at pressures below 1.3×10^{-3} Pa. Their tendency for puffing was not as high and they sublimed with relatively steady rates.

After the starting materials were purified, they showed much improved sublimation characteristics, which then were very similar for all the phthalocyanines studied. The outgassing time was reduced below 5 min for the first heating cycle

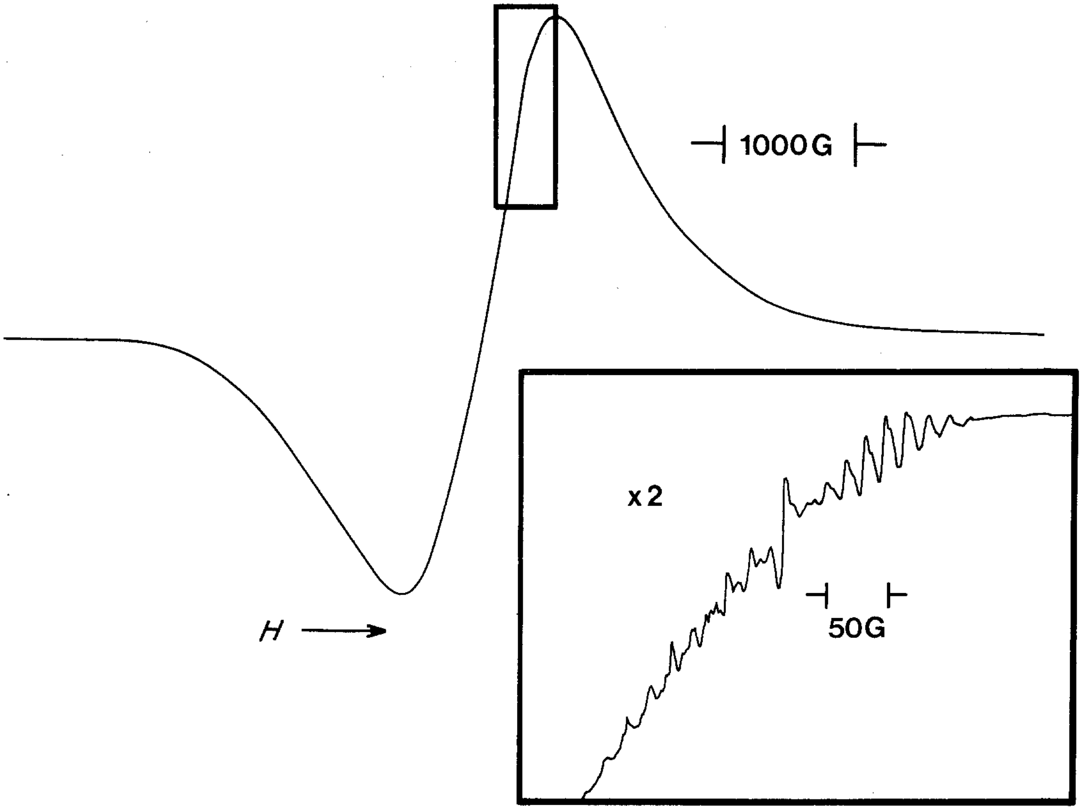

Figure 6 EPR spectrum of x-H_2Pc before purification (the amplitude of the inset is magnified 2 times).

and to practically zero for subsequent sublimations. Usually the pressure remained below 1.3×10^{-4} Pa. In some cases sublimations were performed at 2×10^{-5} Pa. The onset of sublimation was very sharp and once a certain evaporation rate was established it remained relatively stable. Puffing of a purified material occurred only in one case where the deposition rate was very high ($\geqslant 1.4\,\mathrm{nm\,sec^{-1}}$); it never happened during normal operations with rates around 0.2 to $0.5\,\mathrm{nm\,sec^{-1}}$. No black residue was found in the boats after the phthalocyanines were sublimed.

A sample of the VOPc, used to prepare Cell 3 (Table II), was vacuum sublimed in order to check whether the acid pasting had adverse effects on the improved characteristics. But no change in sublimation behaviour was observed.

3.6. Effect of repeated purification

In order to study the effect of repeated purification, a sample of already purified ZnPc was sublimed a second time.

In this case the starting material sublimed completely and nearly all of it deposited again as ZnPc, i.e. no residue was left behind and no impurity depositions were observed. The optical absorption of the ZnPc after this second purification was identical with that of the starting material. The photosensitivity improved only slightly by less than 10% and the vacuum sublimation behaviour did not change at all [19].

No X-ray analysis or EPR study of this sample were made.

4. Discussion and conclusions

The results showed clearly that the train sublimation procedure is a simple and effective method to purify organic pigments.

The spectroscopic characterization of the purified materials from both zones indicated that all phthalocyanine deposits are of the β-modification with the exception of VOPc and MgPc. VOPc deposited in phase II.

In case of MgPc a new polymorphic form was discovered which exhibits an absorption maximum at 850 nm (Fig. 4c). Effects of light scattering can be ruled out as the origin of this line because they should also create additional structures in the spectra of H_2Pc, ZnPc and CuPc which were not observed. This result and the fact

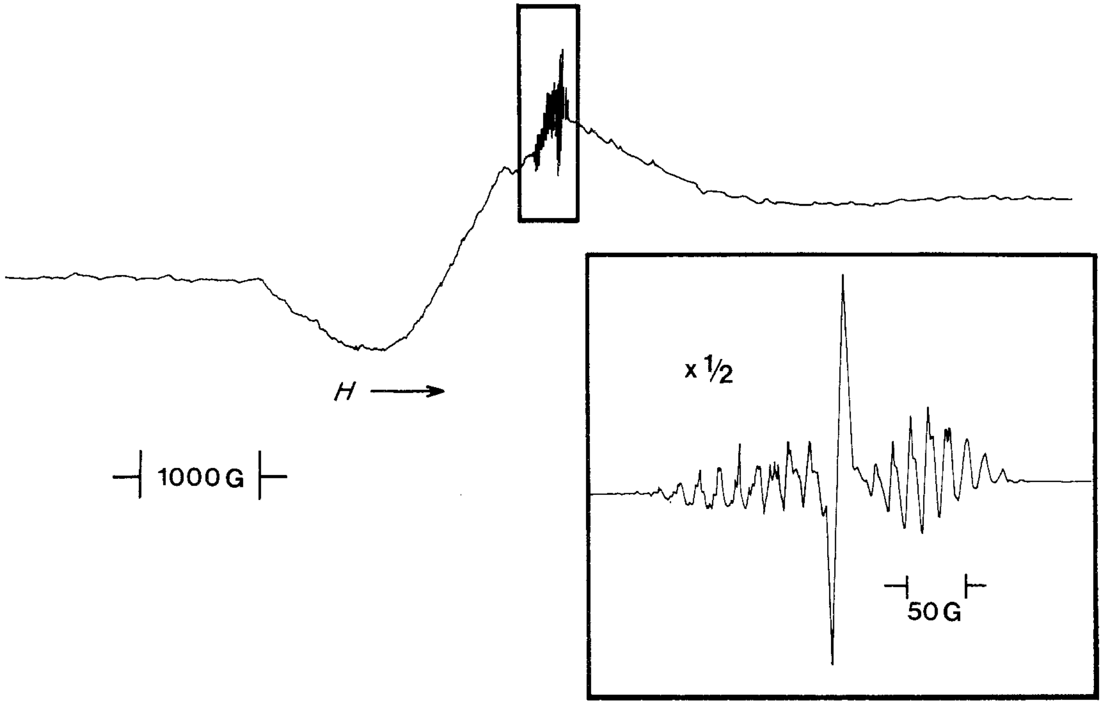

Figure 7 EPR spectrum of H_2Pc purified from x-H_2Pc (the amplitude of the inset is reduced by one half).

that a similar additional absorption line was seen in a sublimed MgPc film (Fig. 8), suggest strongly the existence of a second phase. From VOPc it is well known that such a second phase can give rise to an additional near infrared absorption band. However, additional evidence is still needed to establish the existence of phase-II-MgPc beyond doubt.

In the case of PbPc a comparison with other workers' results is difficult, because little has been published regarding the structure of this material. The unit cell dimensions given in Section 3.2 are quite different from those reported by Ukei [20], who found a distance of only 0.373 nm between neighbouring Pb atoms along the stacking axis of the molecules. It remains to be seen whether this discrepancy is a result of a difference in modification; further work along this line is in progress.

TABLE III Change in vacuum sublimation characteristics of MgPc

Characteristic	Unpurified	Purified
Pressure	$\geqslant 3.3 \times 10^{-3}$ Pa	$\sim 5 \times 10^{-5}$ Pa
Outgassing	1 h to 15 min	5 min to 0 min
Onset of sublimation	broad current range (10 A)	sharply defined ($\frac{1}{2}$ A)
Rate of sublimation	fluctuates and changes	very steady
Puffing of material	occurs readily	occurs very seldom
Residue after sublimation	some black fluffy powder	none

The EPR results show a definite removal of impurities only in the case of PbPc and ZnPc. These materials are diamagnetic, therefore the large signals found in the unpurified samples had to be due to paramagnetic impurities. The much smaller spin concentrations in the purified materials prove that a considerable part of the impurities is indeed removed. Metal-free phthalocyanine changed from the x- to the β-form during the zone refining process, and therefore the observed increase in free spin concentration can be caused by two mechanisms, either

(a) creation of decomposition products due to the high sublimation temperature, or

(b) formation of structural disorder which accompanies the modification change.

The latter mechanism, according to [15], should dominate in this case, because the transition occurs from a highly ordered phase (x-form) to a usually very disordered polymorph (β-form).

Boas *et al.* [10], however, found that their observations on the purification of "ordinary" H_2Pc could be explained satisfactorily with

Mechanism (a). Analogue reasoning, i.e. the increase of free spin density due to decomposition products, can be applied to describe the EPR results of VOPc and MgPc (Table I). In case of MgPc the analogy goes even further because of the linear relation between the free spin concentration and the purification temperature, mentioned in Section 3.3, which was also reported in [10] for H_2Pc.

The creation of spins during the train sublimation of H_2Pc, VOPc and MgPc most likely obscured any removal of impurities which might have occurred simultaneously. This is certainly the case for MgPc and VOPc because these materials are paramagnetic themselves and therefore the removal of paramagnetic impurities is not expected to influence the EPR signal to any great extent.

Because the EPR spectra of CuPc exhibited dissimilar characteristics it was not possible to compare the areas under the absorption lines. Therefore, no information regarding a change of impurity concentration could be obtained. From these results it becomes obvious that EPR spectroscopy cannot be used to assess the efficiency of the purification process on H_2Pc, VOPc, MgPc and CuPc.

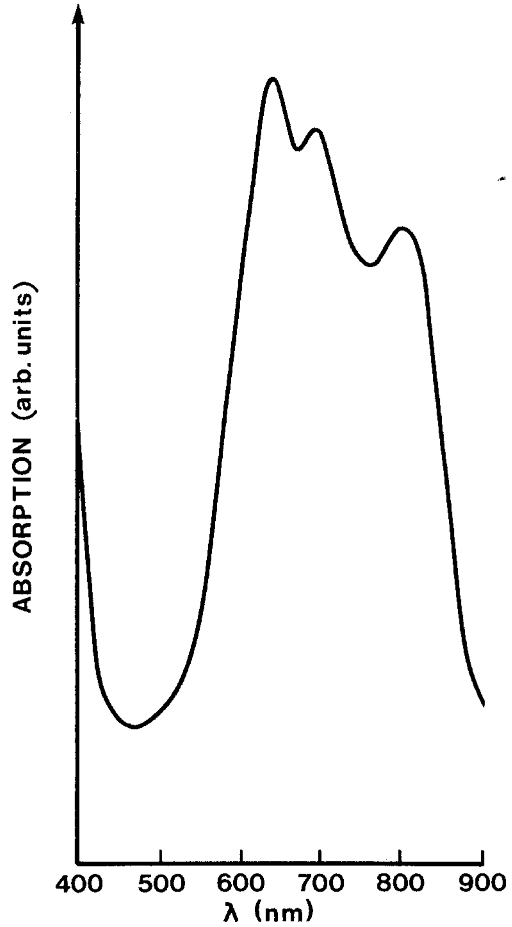

Figure 8 Absorption spectrum of a vacuum sublimed MgPc film, 260 nm thick.

The positive effects of the purification on the phthalocyanines is demonstrated most impressively by the improvement of the vacuum sublimation properties and the increase in photosensitivity. The latter effect has only been studied for VOPc, but there is no obvious reason why the other materials should behave differently.

One of the most striking differences in the sublimation behaviour is the considerable reduction of the outgassing time. If this was caused simply by a decrease in surface area due to the formation of crystallites, then the old outgassing behaviour should reappear once the particle size is reduced to the original dimensions. One way this can be achieved is to acid paste the purified material, which has been done in case of VOPc to prepare Cell 3. However, the sublimation characteristics of this material did not change. Hence the decrease in outgassing is clearly a result of the increased purity of the phthalocyanines due to the train sublimation.

From the results of the study of repeated purifications of ZnPc, we conclude that practically all impurities are removed during the first train sublimation. As we are primarily concerned with photovoltaic applications of phthalocyanines, we feel that the nearly negligible increase in photosensitivity due to a second sublimation step would not justify the additional time and costs involved.

5. Summary

The technical details of a simple zone refining system have been described. H_2Pc, CuPc, VOPc, ZnPc, MgPc and PbPc were purified and characterized by several techniques. The results show that most of the impurities contained in the starting materials are removed in one purification step resulting in a considerable improvement of the material characteristics. Some evidence for a second phase in MgPc has been found.

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