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PHYSICOCHEMICAL AND DYEING PROPERTIES OF PIGMENTS CONTAINING 3- OR 4-AMINOPHTHALIMIDE RESIDUE

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SUMMARY

Several monoazo pigments containing the residues of 3-aminophthalimide and its N-methyl and N-phenyl derivatives in the pigment molecule have been prepared. Their physicochemical and fastness properties were examined and compared with those of analogous 4-aminophthalimide pigments

Based on the observed differences in physicochemical properties and different solvent stabilities, it is suggested that the 3-aminophthalimide pigments form mostly intra-molecular hydrogen bonds whereas the 4-aminophthalimide pigments form mainly inter-molecular hydrogen bonds. The hypothesis has been verified by the IR and UV spectra of 3- and 4-acetylaminophthalimide and of their N-methyl derivatives as model compounds

1 INTRODUCTION

One of the most important properties of pigments is fastness to water and organic solvents, together with heat stability For several years a great deal of information about pigments with regard to those properties has been published, especially in the form of patents Usually, trial-and-error methods have been used to select a range of good pigments, since despite many investigations there is still a lack of conclusive generalizations enabling the properties of dyes of specified structure to be foreseen Hitherto theoretical studies have not sufficiently explained the relationship between the structure and properties of pigments It was, therefore, decided to attempt some further elucidation of this problem

In the synthesis of inexpensive and stable azo pigments, the view has been put forward by Gaertner[1] that the poor solubility and high melting point, and

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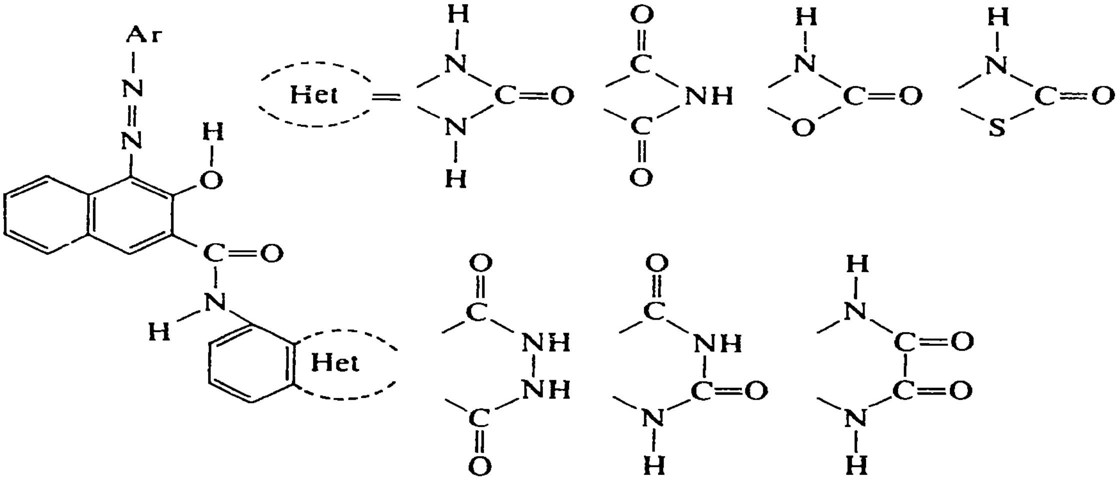
consequently the solvent and heat stabilities of a pigment are due to its high molecular weight. This view has been discussed by Kraska[2] who pointed out the fact that apart from the molecular weight, it is the flat, linear and symmetric structure of a pigment molecule which is of great importance in imparting the required characteristics to pigments (i e. low solubility and high melting point). One solution of the problem was a trend to synthesize at least disazo pigments This often resulted in difficulties because of formation of increased amounts of monoazo by-products Another difficulty often came from the necessity to use thionyl chloride in the pigment synthesis, an agent which is very corrosive for equipment and hazardous for personnel health The synthesis of disazo Cromophtal pigments (Ciba-Geigy) is a typical example of the situation

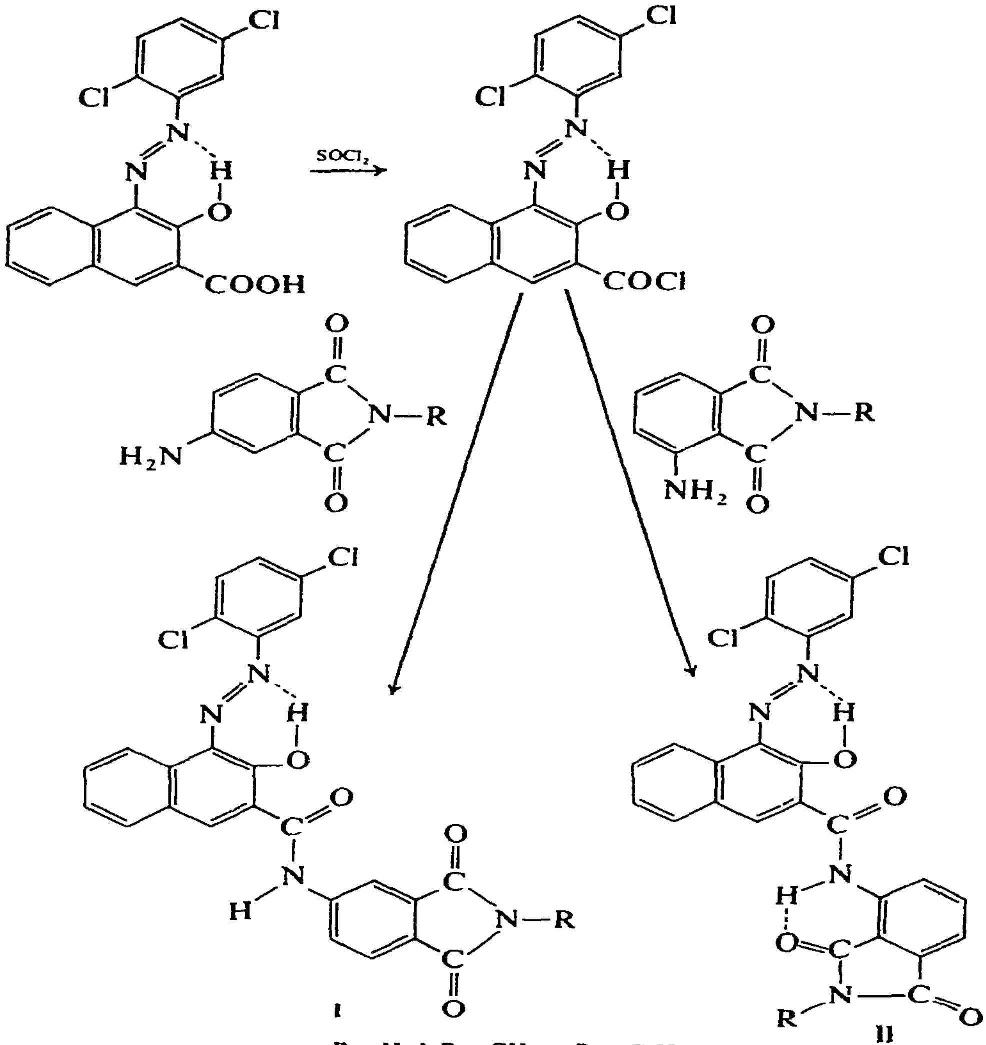
One of the approaches designed to overcome the difficulties comprised the use of anhydrides of *ortho*-[3-5] or peri-dicarboxylic acids[6-8] for the synthesis of disazo pigments Pigments of this type have also been studied by us.[9-11] Using the anhydrides instead of acid chlorides, it is possible to avoid the troubles resulting from the use of thionyl chloride However, in spite of numerous trials, it has not been possible to eliminate the formation of readily soluble monoazo compounds or non-cyclized by-products containing carboxylic groups

While most of the pigment producers endeavoured to improve the manufacturing processes for disazo-pigments, Hoechst introduced stable Hostaperm and PV-Echt pigments into the market [12] Although monoazo, the pigments turned out to be as stable as the disazo Cromophtal pigments. These compounds were often more stable than those prepared by us,[9-11] i e phthalimide and naphthalimide based disazo-pigments of similar structure A common feature of all the useful pigments in this connection is the presence of a heterocyclic amide residue in the molecule [12-15]



The effect of heterocyclic amide groups in the dye molecule has not been fully explained; however they seem to promote in the azo-pigments a flat structure and considerable association by means of hydrogen bonds or other inter-molecular interaction, similarly to other stable pigments.[16]

In order to explain clearly the consequence of the —CO—NH— group in the heterocyclic arrangement, several pigments, derivatives of phthalimide having various substituents at the heterocyclic nitrogen atom, have been prepared and



a R = H, b R = CH_3, c R = C_6H_5

investigated The use of phthalimide derivatives as a subject of studies instead of the popular benzimidazolone radicals was considered reasonable because of the wide availability of suitable *N*-substituted derivatives

The pigments containing 4-aminophthalimide residue (**I**) have been studied previously[17] It was found that the presence of unsubstituted imide group (**Ia**) in the pigment provided solvent and heat stabilities (low solubility and high melting and degradation points)

Analogous pigments containing substituted imide group, **Ib** and **Ic**, in spite of higher molecular weights, show lower solvent stabilities and somewhat lower melting points

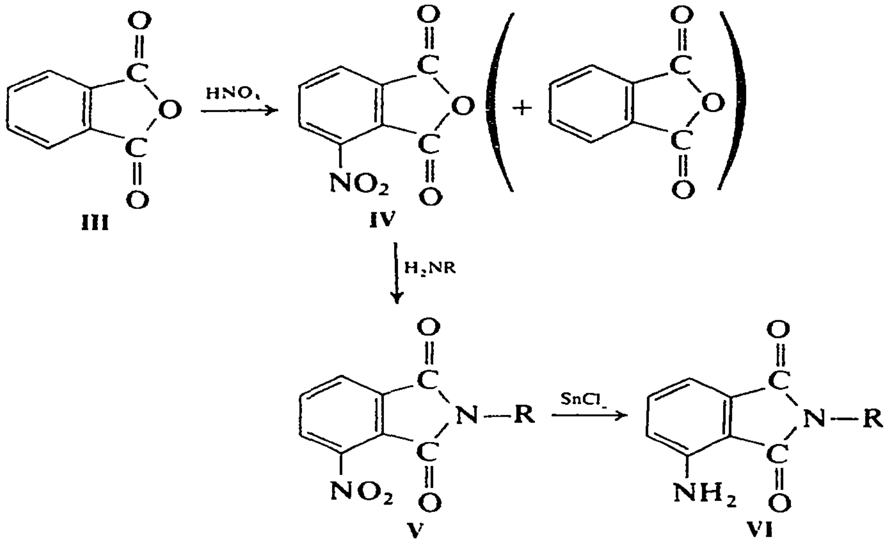
Investigations carried out with phthalimide and naphthalimide as model compounds[18] have shown that the relevant pigments properties are due to a strong self-association of their molecules through hydrogen bonds This has been additionally confirmed by X-ray radiographic studies on the crystal structure of phthalimide[19] and naphthalimide[20] It was found in both cases that the fundamental element of the crystal structure is a dimer combined by hydrogen bonds N—H O of 2 895 Å and 2 85 Å in length Similar type dimers as basic crystal components have been recently found in one of the benzimidazolone pigments[21]

In practice, instead of phthalimide derivatives, other different compounds containing heterocyclic amide arrangements are usually used for the synthesis of pigments The position of the —NH—CO— group in these compounds is not the same as that in the 4-aminophthalimide derivatives Therefore, to obtain clearer information, it seemed useful to extend the investigations to use the isomeric 3-aminophthalimide and its *N*-methyl or *N*-phenyl derivatives Using the methods described previously,[17] three suitable 3-aminophthalimide pigments (**II**) having different substituents in the imide residue (**a**, R = H, **b**, R = CH_3, **c**, R = C_6H_5) were prepared The properties of the prepared pigments were compared with those of previously examined isomeric 4-aminophthalimide derivatives, and considerable differences were found, as expected, which were due to different position of acylamine residue in the pigment molecule

2 EXPERIMENTAL

3-nitrophthalic anhydride (**IV**) was prepared by nitration of phthalic anhydride (**III**) as described by Culhane[22] The product was used to prepare 3-aminophthalimide (**VIa**), 3-amino-*N*-methylphthalimide (**VIb**) and 3-amino-*N*-phenylphthalimide (**VIc**) according to the following scheme, using similar conditions of acylation and reduction as those in the synthesis of 4-aminophthalimide[17]

Pigments **II** were prepared and purified as pigments **I** described previously,[17] starting with suitable 3-aminophthalimide derivatives



(a) R = H (b) R = CH_3 (c) R = C_6H_5

Melting points (uncorrected), were determined with a Boetius HMPK 05 apparatus

Thermal analysis of pigments was carried out in air at temperatures up to 800 °C with a Paulik, Paulik, Erdey derivatograph (MOM-Budapest), using a specimen of 60 mg at a heating rate of 7 9 °C min^{-1}†

IR absorption spectra were obtained with Specord 71-IR and UR-10 spectrophotometers (Zeiss Jena). The absorptions of samples were measured in the crystalline form, using powdered mixtures with KBr The molar extinction of cyclohexane–dioxane solutions of *N*-acetylaminophthalimides versus dioxane concentration was examined by the modified[18] method of Forbes.[23]

The stability of pigments was examined according to the Polish Standards which are much the same as the British Standards

Light-fastness of dyeings was measured with Xenotest apparatus (Hanau)

3 RESULTS, DISCUSSION AND CONCLUSIONS

Several 3-aminophthalimide derivative pigments (II) were synthesised and their physicochemical and fastness properties were examined and compared with those of analogous 4-aminophthalimide (I) derivative pigments, investigated previously

It is seen from Table 1 that all the pigments based on 3-aminophthalimide (II)

† We are grateful to Dr G Janowska for thermograms made in Polymer Institute Polytechnical University, Łodz

TABLE I

MELTING AND DECOMPOSITION POINTS AND FASTNESS OF PIGMENTS

Pigment	*R*	*m p* (°C)	*DTA data*				*Fastness to solvents*					
			m p (°C)	% *decomp*	*max decomp point* (°C)	% *decomp*	*Ethanol*	*Acetone*	*Ethyl acetate*	*Xylene*	*Chlorobenzene*	*Butyl phthalate*
Ia	H	358-360	365	21	570	90	5	5	5	5	5	5
Ib	CH_3	338-340	350	23	560	92	5	4-5	4-5	4	3-4	5
Ic	C_6H_5	336-338	350	18	570	96	4-5	4-5	4-5	4	3-4	4-5
IIa	H	263-264	265	18	620	96	5	4-5	4-5	4	4	5
IIb	CH_3	267-268	280	17	620	95	5	4-5	4-5	4	4	5
IIc	C_6H_5	262-263	270	18	610	96	5	5	4-5	4	4	5

have melting points lower by about 100 °C than those of the 4-aminophthalimide pigments (**I**). There is no distinct decrease in the melting point of *N*-substituted 3-aminophthalimide pigments (**IIb** and **IIc**), unlike that to be seen with the 4-aminophthalimide derivatives which show a decrease of about 15 °C. One of the pigments containing the 3-amino-*N*-methylphthalimide residue (**IIb**) even has a melting point somewhat higher than that of the pigment containing an unsubstituted phthalimide residue (**IIa**)

On melting, all the examined pigments undergo partial decomposition or sublimation (loss of weight about 20 %). A complete decomposition (about 95 % of weight loss) takes place on heating to temperatures above 500 °C. There is no distinct effect due to the type of substituent in the imide residue on the decomposition temperature

Similar conclusions may be drawn from the results of solvent stability determinations (Table 1) The solvent stability of pigments based on 4-aminophthalimide (**I**) depends on the type of substituent R in the phthalimide residue. The pigment containing an unsubstituted NH group (**Ia**) has a higher stability by 0·5 to 1·5 fastness points as compared with the pigments with an NCH_3 (**Ib**) or NC_6H_5 group (**Ic**). On the other hand, the type of substituent R makes no difference with 3-aminophthalimide pigments (**II**). (An interesting observation which is difficult to explain at present, is the lower light-fastness of dyeings made with these pigments on a poly(vinyl chloride) film.)

All the above observations lead to the conclusion that the differences in properties of 3- and 4-aminophthalimide pigments are due to different types of hydrogen bonds formed by these compounds It is most likely that the 3-aminophthalimide derivative pigments with their stable intra-molecular hydrogen bonds (—C═O ·H—N—), have a low degree of inter-molecular association, while the 4-aminophthalimide pigments form only inter-molecular hydrogen bonds and, hence, they are considerably associated

This view is confirmed by the IR spectra of the pigments (Table 2) The spectra of 3-aminophthalimide pigments (**IIa**) reveal a very weak bond characteristic for the associated NH group (3300 cm^{-1}), while the corresponding bond in the spectra of 4-aminophthalimide pigments is very clear and shifted bathochromically

TABLE 2
IR SPECTRA OF PIGMENTS

Pigment	*R*	$\nu_{C=O}$ (cm^{-1})			ν_{NH} (cm^{-1})	
Ia	H	1688	1724	1770	3220	3440 w
Ib	CH_3	1680	1710	1760	—	3420 w
Ic	C_6H_5	1682	1718	1762	—	3420 w
IIa	H	1680	1732	1770	3300 w	3450 w
IIb	CH_3	1680	1710	1740	—	3400
IIc	C_6H_5	1684	1720	1745	—	3400

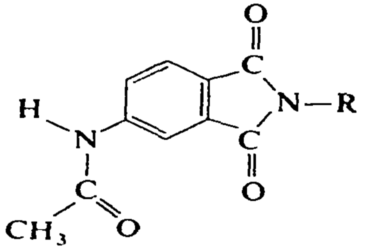
(3220 cm^{-1}) On the other hand, there are no distinct differences in the bond positions within the range of CO vibrations, the only change being in their intensities The interpretation of IR spectra is made difficult by the fact that in the pigment molecules, beside the hydrogen bonds formed via NH groups, there are strong hydrogen bonds between hydroxyl and azo groups (as shown in patterns **I** and **II**)

TABLE 3

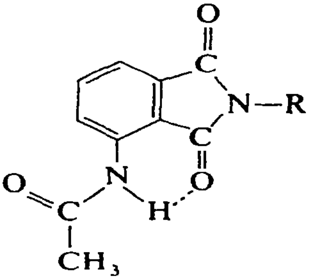
IR SPECTRA OF *N*-ACETYLAMINOPHTHALIMIDE DERIVATIVES

Compound	*R*	$\nu_{C=O}$ (*cm*$^{-1}$)			ν_{NH} (*cm*$^{-1}$)	
VIIa	H	1681	1715	1778	3170	3320
VIIb	CH_3	1692	1715	1765	—	3350
VIIIa	H	1695	1723	1770	3060-3120-3165	3360
VIIIb	CH_3	1697	1712	1765	—	3370

Additional arguments confirming the view about the intra- and inter-molecular nature of interactions in the pigments under investigation are provided by the IR and UV spectra of 4-*N*-acetylaminophthalimide (**VII**) and 3-*N*-acetylphthalimide (**VIII**) as well as of their *N*-methyl derivatives treated as model compounds (Table 3) with the same tendency to form or not to form inter- and intra-molecular hydrogen bonding as the pigments (**I**) and (**II**)



VII



VIII

(**a**) R = H, (**b**) R = CH_3

The IR spectra of the model compounds reveal bands similar to those of corresponding pigments Very clear differences are observed in the shape of curves illustrating the dependence of the molar absorption coefficient (ε_{max}) on the dioxane content in cyclohexane–dioxane solutions of *N*-substituted and unsubstituted 3- and 4-*N*-acetylaminophthalimide derivatives The curves of $\varepsilon_{max} = f(c_{DIOX})$ for the unsubstituted phthalimide derivatives (Fig 1—**VIIa** and **VIIIa**) are very similar in shape and are consistent with the presence of associated molecules in which hydrogen bonding probably occurs between the —$NHCOCH_3$ and —CO—NH—CO

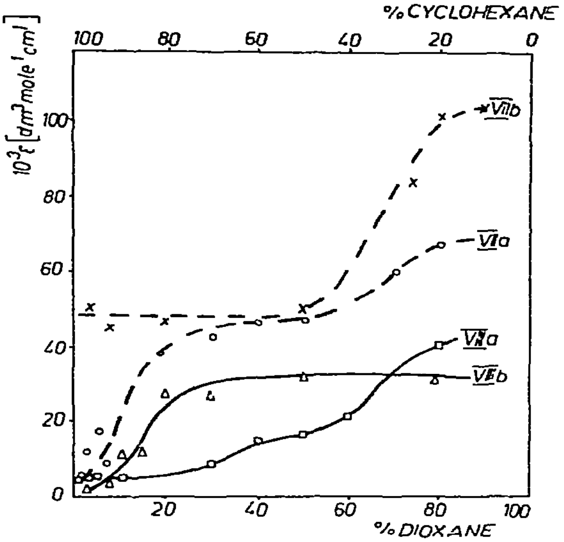


Fig 1 Molar absorption coefficient versus percentage content of dioxane in cyclohexane–dioxane solutions of *N*-acetylaminophthalimides

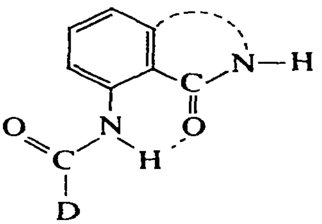
groups The analogous plots for the *N*-methyl derivatives (Fig 1—**VIIb** and **VIIIb**) are, on the other hand, more characteristic of less associated compounds The high value of ε_{max} (relative to that of **VIIIa**) of the 3-acetylamine-*N*-methylphthalimide solutions (Fig 1—**VIIIb**) at lower dioxane content is consistent with the presence of a largely non-associated product, the ε_{max} value of which is little affected by further dioxane addition This may be explained by the increased ability of 3-acetylamine-*N*-methylphthalimide (**VIIIb**) to form an intra-molecular hydrogen bond and hence the lower ability to develop inter-molecular association. The quantitative measurement of association was made difficult by the low solubility of both the pigments and the model compounds

It was found that the 4-aminophthalimide pigments have higher melting points and somewhat better solvent stability than the analogous 3-aminophthalimide derivatives The IR spectra of the pigments and model compounds also show that the 4-aminophthalimide derivatives are associated to a higher extent

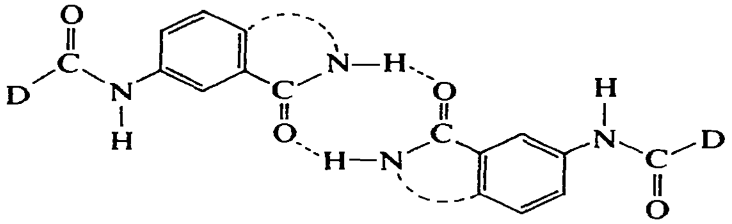
The results of the present investigations suggest that monoazo pigments containing heterocyclic amide substituents are characterized by unexpected heat and organic solvent stabilities owing to self-association by means of hydrogen bonds, but the ease of formation and stability of the associates depends on the position of acylamine group in the pigment molecule

In order to prepare good pigments containing the heterocyclic amide system such starting products which would provide stable self-association by means of hydrogen bonds have to be used. Thus, the use of *N*-substituted amide systems is of little value

It is important to locate the acylamine group in *meta* or *para* position relative to the carbonyl group, rather than the *ortho* position, so as to preclude the formation of a 'competitive' intra-molecular linkage Owing to such structures, the dimensions of pigment molecules are twice as large, and the flat structure of associates provides possibilities for further mutual interactions with molecules of pigment in crystals



no inter-molecular interaction



dimerization

Based on the above considerations, it is possible to forsee which of the starting materials containing heterocyclic amide systems will be useful and which should be avoided

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