

CHROM. 5813

Identification of organic compounds

LXXVII*. Paper and thin-layer chromatography of azo pigments

Organic pigments used for dyeing rubber, plastics, printing inks, lacquers and paints are mainly azo dyes, derivatives of anthraquinone, phthalocyanines or vat dyes. All are practically insoluble in water and only some of them are soluble in high boiling organic solvents at elevated temperatures. This might have caused some difficulties in connection with the application of chromatographic methods to their separation. Only a few authors have tried to use paper (PC) and thin-layer chromatography (TLC)¹⁻⁴. In our laboratory, the scope and limitations of PC and TLC for the separation and identification of azo pigments were investigated and the results are summarized in this paper.

Experimental

Thin-layer chromatography. All experiments were carried out on commercially available silica gel sheets: Silufol (Kavalier, Czechoslovakia), MN-Polygram Sil G-254 UV (Macherey, Nagel and Co., Düren, G.F.R.) and DC-Alufolien Kieselgel (Merck, Darmstadt, G.F.R.). There was no difference in the accuracy of the results obtained with these three materials.

Pigments were applied in the form of saturated solutions in warm dimethylformamide. After application, the spots were dried with a stream of warm air from a hair dryer for 30 min. Benzene and toluene were used as mobile phases.

Paper chromatography. Whatman No. 3 paper was used.

Azo lakes were applied in the form of saturated solutions in warm dimethylformamide or in aqueous pyridine after boiling for several minutes. The spots were dried in a stream of warm air. The following mobile phases were used: 1-propanol-ammonia (2:1) and 1-propanol-*n*-butyl acetate-ammonia (2:1:1).

Results and discussion

From the point of view of their chemical structures, azo pigments belong to one of the following groups:

- (1) Pigments containing acetoacetarylamides.
- (2) Pigments containing 2-naphthol.
- (3) Pyrazolone azo dyes.
- (4) Pigments containing arylamides of 2-hydroxy-3-naphthoic acid.
- (5) Lakes of azo dyes containing carboxy and/or sulpho groups.

Our preliminary experiments have shown that each of the groups under consideration should be approached separately. It has also been found that the choice of an appropriate solvent for application of the pigments to the starting points of the chromatograms is a very important problem common to all these groups of azo pigments. Dimethylformamide was found to be a suitable solvent. The solutions of pigments prepared at elevated temperatures were so strongly coloured that only small volumes

* Part LXXVI: *Chem. Listy*, in press.

TABLE I

 R_F VALUES OF YELLOW AZO PIGMENTS

TLC on Silufol sheets; mobile phase: benzene.

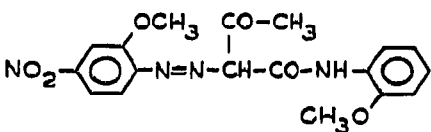
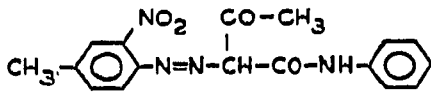
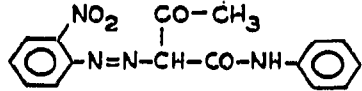
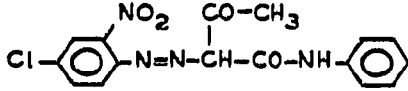
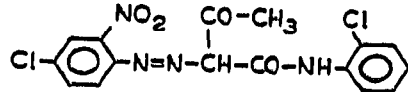
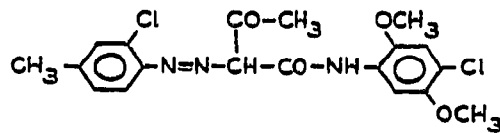
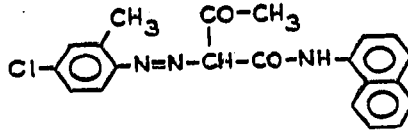
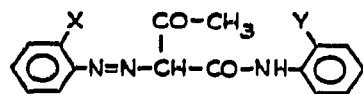
Formula	Colour index No.	R_F values
		0.17
	11680	0.24
	11660	0.26
	11670	0.26
	11710	0.47***
		0.38
		0.65

TABLE II

 R_F VALUES OF SUBSTITUTED BENZENEAZOACETOACETANILIDES

TLC on Silufol sheets; mobile phase: benzene.

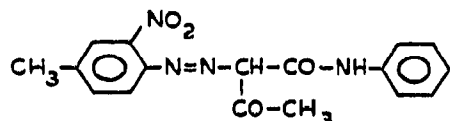


Pigment	Substituents		R_F values
	X	Y	
I	H	H	0.38
II	H	CH ₃	0.35
III	CH ₃	H	0.43
IV	H	Cl	0.44
V	Cl	H	0.46
VI	H	OCH ₃	0.22
VII	OCH ₃	H	0.29

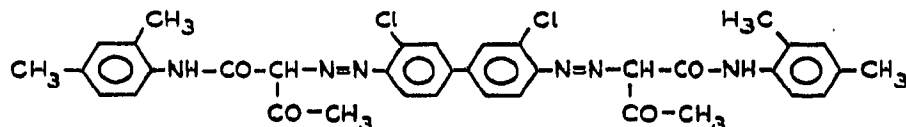
could be applied to the chromatograms. Boiling in aqueous pyridine was another suitable method for the preparation of solutions of some of the lakes.

The application of these solutions to the chromatograms must be carried out with great care. In particular, the drying of the starting points after the application of the solutions is of great importance because the dimethylformamide remaining on the starting points could have an unfavourable influence on the migration and the shapes of the pigment spots that have lower R_F values. Fig. 1 represents a chromatogram on which the same volumes of a solution of a brown pigment (Permanent Brown FH) were applied to the three starting points. First the solution was applied to point 1 and the spot was dried in a stream of warm air for 40 min. Then the solution was applied to point 2 and drying of this spot limited to only 5 min. Finally, the solution was applied to point 3 and, without further drying, the chromatogram was immediately developed with benzene. The influence of dimethylformamide on the starting points is evident.

(1) *Pigments containing acetoacetylarnides*. This group of pigments includes monoazo dyes, a typical example of which is Hansa Yellow G:



and disazo dyes derived from 3,3'-dichlorobenzidine, *e.g.*, Permanent Yellow GR:



Monoazo dyes of this series can be dissolved in warm dimethylformamide. The solutions formed are so strongly coloured that it is possible to apply small volumes to the chromatogram. Benzene or toluene can be used as the mobile phase. Sometimes, multiple development with the same mobile phase is advantageous. In Table I, the R_F values of some commercially used pigments are summarized.

We also chromatographed a series of model compounds involving unsubstituted benzeneazoacetoacetanilide and its derivatives containing methyl, chloro, methoxy and nitro groups in different positions on the active or passive coupling component, in order to study the relations between the chromatographic behaviour of these compounds and their chemical structures. We found that the methyl group in any position and chlorine in the *p*-position of the active component have only a small effect. A considerable increase in the R_F values is caused by chlorine in the *o*-position of both coupling components, while the introduction of methoxy and nitro groups results in a considerable decrease in R_F values. The different influence of the same substituent when present in the active or passive coupling component is shown in Table II.

Disazo dyes derived from chlorinated benzidine are only slightly soluble in dimethylformamide. If it is possible to apply them to the starting point, they have lower R_F values. Some of them do not migrate under the experimental conditions used.

(2) *Pigments containing 2-naphthol*. These dyes are derivatives of benzeneazo-2-

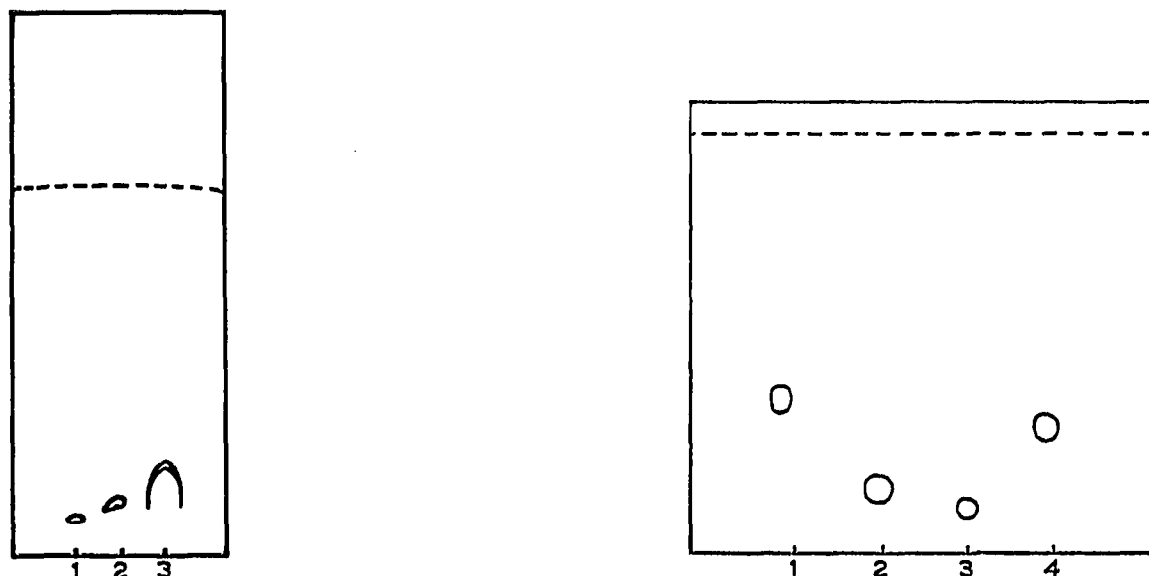
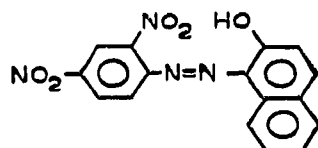


Fig. 1. Chromatogram of Permanent Brown FG applied in dimethylformamide solution on Silufol sheet; mobile phase: benzene. 1 = Dried for 40 min after application; 2 = dried for 5 min after application; 3 = without drying. For explanation, see text.

Fig. 2. Chromatogram of substituted benzeneazo-2-naphthols in dimethylformamide solution on Silufol sheet; mobile phase: benzene. 1 = Sudan I (benzeneazo-2-naphthol); 2 = CI 12075 (2,4-dinitrobenzeneazo-2-naphthol); 3 = CI 12120 (2-nitro-4-methylbenzeneazo-2-naphthol); 4 = CI 12085 (2-chloro-4-nitrobenzeneazo-2-naphthol).

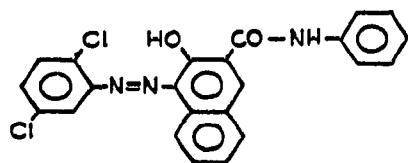
naphthol, the active coupling component of which is substituted by one or two nitro, chloro or methyl groups, *e.g.*, Hansa Orange RN:



These dyes are sufficiently soluble in dimethylformamide and benzene or toluene can be used as the mobile phase for their chromatographic separation. A typical chromatogram is shown in Fig. 2.

(3) *Pyrazolone azo dyes.* Monoazo dyes of this group are very soluble in dimethylformamide. When benzene or toluene is used as the mobile phase, chromatograms with well formed spots are obtained. Permanent Orange G is a disazo pigment of this type and can be chromatographed as well as the monoazo dyes (Fig. 3).

(4) *Pigments containing arylamides of 2-hydroxy-3-naphthoic acid.* A typical example of this group is Permanent Red FRR:



If these pigments are soluble in warm dimethylformamide and can be applied to the chromatogram, good chromatograms are obtained using benzene or toluene as the mobile phase and multiple development when necessary. In comparison with the

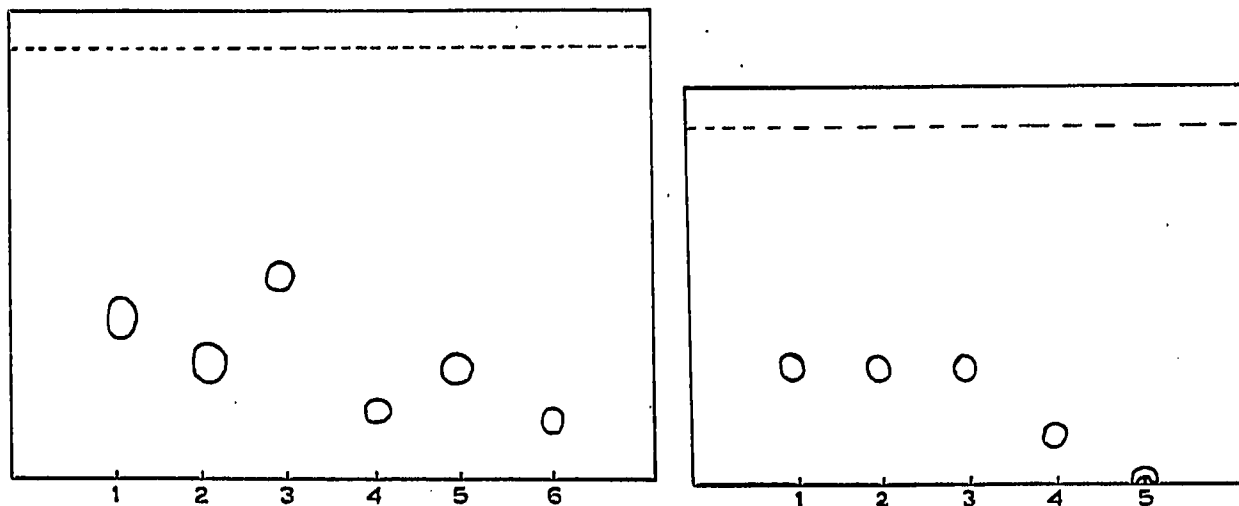


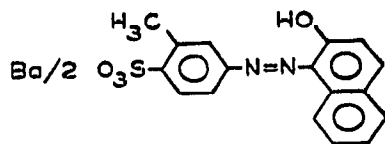
Fig. 3. Chromatogram of azo derivatives of 1-phenyl-3-methyl-5-pyrazolone in dimethylformamide solution on Silufol sheet; mobile phase: benzene. 1 = CI 12705 (2-chlorobenzeneazo derivative); 2 = CI 12720 (2-methylbenzeneazo derivative); 3 = CI 12710 (2,5-dichlorobenzeneazo derivative); 4 = CI 12730 (2-nitro-4-methylbenzeneazo derivative); 5 = unsubstituted benzeneazo derivative; 6 = CI 21110, Permanent Orange G (3,3'-dichlorobenzidine derivative),

Fig. 4. Chromatogram of model azo dyes of groups 1-4 on Silufol sheet; mobile phase: benzene. 1 = Benzeneazoacetanilide (Group (1)); 2 = benzeneazo-2-naphthol (Group (2)); 3 = benzeneazo-1-phenyl-3-methyl-5-pyrazolone (Group (3)); 4 = benzeneazo-2-hydroxy-3-naphth-anilide (Group(4)); 5 = benzeneazo-2-hydroxy-3-naphthoic acid (Group (4)).

preceding groups of pigments, these pigments have lower R_F values. If a further amide group is present in the molecule, the compounds remain at the start.

For comparison of the migration of pigments belonging to groups (1)-(4), model compounds were prepared from diazotised aniline and the corresponding passive coupling components and chromatographed on Silufol sheets as described above. The behaviour of these compounds is evident from Fig. 4.

(5) *Lakes*. Yellow, orange and red pigments of this group contain one carboxy and/or one sulpho group. Furthermore, they contain sodium, barium, calcium, manganese, ect. A typical example is Graphtol Red RMT:



These pigments can be dissolved in dimethylformamide, and in some cases solutions can be prepared by boiling the pigment with aqueous pyridine. Under the conditions suitable for the TLC separation of the preceding groups of pigments, lakes do not migrate at all. Mobile phases such as *n*-butyl acetate-acetic acid-water (4:2.5:1) or 1-propanol-ammonia (2:1) are suitable for their separation. With the former solvent system, good separations of yellow lakes such as Graphtol Yellow GRL-PV, 3 GLN-PV and 3GL-PV are achieved. Very good results can also be obtained by PC using the systems 1-propanol-ammonia (2:1) and 1-propanol-*n*-butyl acetate-ammonia (2:1:1). The first system is especially suitable for the differentiation of lakes with one and two sulpho and/or carboxy groups.

To summarize, it is possible to find in each of the five groups of pigments mentioned dyes that can be chromatographed by using the chromatographic procedures described. The limiting factor is the solubility of the pigments under investigation in warm dimethylformamide. The application of the solutions to the chromatograms must be carried out with great care, and the drying of the spots on TLC sheets represents the factor that considerably influences the results. The methods described have been used for purity control and identification of commercial pigments.

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