A NEW GROUP OF AZOIC PIGMENTS BASED ON THE COUPLING REACTION OF 5-CHLORO-OXINE WITH THE DIAZONIUM SALTS OF AROMATIC AMINES

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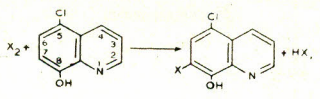
A new group of azoic pigments has been prepared by the coupling reaction of 5-chloro-8-hydroxyquinoline with the diazonium salts of aromatic amines. According to this reaction, aniline, *o*-, *m*-, and *p*-chloroanilines, *o*-, *m*- and *p*-bromoanilines, *o*-, *m*- and *p*-nitroanilines, *p*-aminophenol, 2:4-dichloroaniline, *o*-anisidine, *p*-toluidine, 5-nitro, *o*-toluidine, *p*-aminoazobenzene hydrochloride, *p*-aminodiphenyl, *p*-aminoacetanilide, α-and β-naphthylamines, etc., have yielded such azoic pigments as are mostly deep red in colour.

Introduction

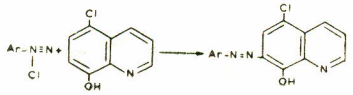
5-Chloro-oxine was prepared from *p*-dichlorobenzene which is a by-product of the D.D.T. manufacture.[1] The chloro-oxine couples with diazotized aromatic amines to form azoic or ingrain pigments. When the coupling reaction is carried out on the fibre, the colour developed is water-washable and is not uniform. However, the pigments have good decorative and protective powers, good brilliance and are fast to light.

These pigments have not so far been synthesised. The position 7 in 5-chloro-oxine is activated by the neighbouring OH group in position 8. Moreover, as the OH group is *o*-and *p*-directing for diazo compounds,[2] and as the *p*-position in the chloro-oxine is already occupied, the coupling occurs in the *o*-position with respect to the OH group or in position 7 of the 5-chloro-oxine. The reactivity of the position 7 in 5-chloro-oxine is illustrated by the following example:



where X is Cl, Br, I, etc.

Because of this reactivity of the molecule, a large number of reactions, leading to the formation of useful products, has been carried out. These products include 5-chloro-7-iodo-oxine,[3] 5-chloro-7-bromo-oxine,[4] 5,7-dichloro-oxine.[5] In the present studies, a new group of azoic pigments has been synthesised by coupling 5-chloro-oxine with the diazotized aromatic amines. Thus



Diazonium chloride of aromatic amine + 5-Chloro-oxine → Azoic pigment

where Ar denotes an aromatic moiety.

The shades and yields of the various pigments obtained by coupling 5-chloro-oxine with the diazonium salts of aromatic amines, are given in Table 1.

TABLE 1.—THE COUPLING REACTION OF 5-CHLORO-OXINE WITH AROMATIC AMINES.

Base	Pigment	Shade	Yield %
Aniline	5-Chloro-7-phenylazo-oxine	Deep red	90
o-Chloroaniline	5-Chloro-7-(2-chlorophenylazo)-oxine	do	85
m-Chloroaniline	5-Chloro-7-(3-chlorophenylazo)-oxine	Red	87
p-Chloroaniline	5-Chloro-7-(4-chlorophenylazo)-oxine	Deep red	88
o-Bromoaniline	5-Chloro-7-(2-bromophenylazo)-oxine	Red	85
m-Bromoaniline	5-Chloro-7-(3-bromophenylazo)-oxine	do	84
p-Bromoaniline	5-Chloro-7-(4-bromophenylazo)-oxine	do	85
o-Nitroaniline	5-Chloro-7-(2-nitrophenylazo)-oxine	Deep red	82
m-Nitroaniline	5-Chloro-7-(3-nitrophenylazo)-oxine	do	82
p-Nitroaniline	5-Chloro-7-(4-nitrophenylazo)-oxine	do	83
p-Aminophenol	5-Chloro-7-(4-hydroxyphenylazo)-oxine	Dirty-brown	64
2,4-Dichloroaniline	5-Chloro-7-(2,4-dichlorophenylazo)-oxine	Deep red	86
o-Anisidine	5-Chloro-7-(2-methoxyphenylazo)-oxine	do	85
p-Toluidine	5-Chloro-7-(4-methylphenylazo)-oxine	do	87
5-Nitro-*o*-toluidine	5-Chloro-7-(2-methyl-4-nitrophenylazo)-oxine	do	84
p-Aminoazobenzene-hydrochloride	5-Chloro-7-(4-benzeneazophenylazo)-oxine	Reddish brown	67
p-Aminodiphenyl	5-Chloro-7-(4-diphenylazo)-oxine	Deep red	60
p-Aminoacetanilide	5-Chloro-7-(4-acetimidophenylazo)-oxine	Reddish brown	75
α-Naphthylamine	5-Chloro-7-(1-naphthylazo)-oxine	Deep red	82
β-Naphthylamine	5-Chloro-7-(2-nahthylazo)-oxine	do	82

Table 2. Concentrations and Conditions for the Coupling Reaction of 5-Chloro-oxine.

Base								Coupler			
Hydrochlorides of the aromatic amines					Sodium nitrite 1N			5-Chloro-oxine soln			
Aromatic amines	Amount of amines (g)	Conc HCl (ml)	Water (ml)	Temp (°C)	Vol used (ml)	Temp (°C)	Ref	5-Chloro-oxine (g)	NaOH (g)	Water (ml)	Na_2CO_3 (g)
Aniline	10	24	130	0	100	0	6	19	12.5	350	—
o-Chloroaniline	12.8	30	350	2	100	2	6	21	6.5	500	7
m-Chloroaniline	12.8	30	350	2	100	2	6	21	6.5	500	7
p-Chloroaniline	12.8	30	350	2	100	2	6	21	6.5	500	7
o-Nitroaniline	7.0	25	200	5	55	3	6	10.5	5.0	200	5.5
m-Nitroaniline	13.8	50	300	5	110	3	—	21	11	450	10.5
p-Nitroaniline	13.8	50	300	5	110	3	6	20.5	11	450	10.5
o-Bromoaniline	8.6	20	250	2	70	0	—	12.5	5	250	5
m-Bromoaniline	8.6	20	250	2	70	0	—	12.5	5	250	5
p-Bromoaniline	8.6	20	250	2	70	0	—	12.5	5	250	5
p-Aminophenol	10.9	35	200	1	75	1	—	21.5	7	350	8
2,4-Dichloroaniline	16.2	50	250	7	100	4	6	19.5	6.5	350	10.5
o-Anisidine	12.3	30	250	2	100	0	—	21	5.5	300	6.5
p-Toluidine	10.7	30	250	5	100	2	—	20	6	350	6.5
5-Nitro-*o*-toluidine	8.0	20	250	5	70	2	6	12	4	300	4.5
p-Aminoazobenzene	12.7	6.5	300	0	100	0	6	13.5	6	300	—
p-Aminodiphenyl	8.5	25	250	4	80	2	6	14	6	300	5.5
p-Aminoacetanilide	7.5	20	250	2	75	2	—	14.5	6.5	350	4.5
α-Naphthylamine	14.3	22	120	7	6.9 g	5	6	21	7.5	350	5
β-Napthylamine	14.3	22	120	7	6.9 g	5	6	21	7.5	350	5

Experimental

General Procedure.—The aromatic amines were treated with hydrochloric acid to form water-soluble salts. The salts were dissolved in water, cooled to 7–0° and treated with sodium nitrite solution previously cooled to 5–0°, to obtain the diazonium salt solutions. In the diazotization of α-and β-naphthylamines, solid sodium nitrite was used instead of aqueous sodium nitrite.[6]

5-Chloro-oxine was heated to boiling with dilute sodium hydroxide solution and filtered hot. The clear solution was made strongly alkaline by adding sodium carbonate and the solution was cooled to room temperature.

The diazonium salt solution was added dropwise to the 5-chloro-oxine solution with constant stirring of the reaction mixture, when a precipitate of the pigment was obtained. The precipitate was filtered off, washed with water several times and dried.

The reaction conditions, with concentrations of the reagents are enumerated in Table 2.

Discussion

Most of the azoic pigments obtained from 5-chloro-oxine have good covering powers. They are insoluble and compatible with vehicles. Since the soap fastness, the light fastness and the heat resistance of these pigments are also excellent, they can be used successfully in the paint industry.

At present, almost all the pigments consumed in the paint industry of Pakistan are being imported, involving the expenditure of a large amount of foreign exchange. 5-Chloro-oxine can be prepared most economically from the waste of D.D.T. manufacture, which is available in the country.

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