Reactive Heterocyclic Diazonium Treating Agents for InkJet and Other Pigment Applications

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Abstract

Diazonium surface treatment chemistry for Carbon Black and color pigments, invented and developed at Cabot is further expanded by including certain very reactive diazonium compounds, based on electron-deficient heterocycles. Increased reactivity of these molecules vs. aromatic amines significantly expands the range of treatable pigments and provides many choices in generation of InkJet and other high-performance pigment dispersions. Synthetic flexibility of combining a heterocycle with a functional group leads to large number of surface functionalization opportunities.

Introduction

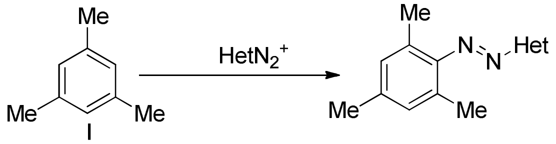
All diazonium treatment reactions for Carbon Black and color pigments, developed at Cabot Corporation until recently were based on benzenoid treating agents, such as sulfanilic acid, p-aminobenzoic acid and the like. Availability of many aromatic amines together with simple methods of their synthesis justified this approach. Reactivity of aromatic diazonium salts and electron-deficient species (cations and/or radicals), derived from these amines is adequate for most treatment cases. It is known[1], that when Carbon Black is treated with diazotized sulfanilic acid, the attachment (calculated as ratio of attached phenylsulphonate to the total) may exceed 80%. However, in the case of the color pigments, due to their decreased reactivity, this value is rarely higher than 10-15%. In case of expensive amines this leads to considerable waste of treating agent and long purification times. For azo pigments, which generally have low reactivity towards electrophilic agents, traditional diazonium treatments are not very effective. Having more reactive agents would open the space to treat a broader class of pigments and increase the amount of surface modification.

Heterocyclic Amines – an Option

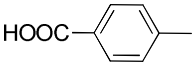
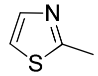
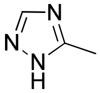
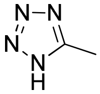
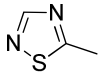
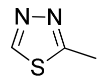
Introduction of pyridine-type nitrogen into an aromatic system leads to significant decrease of nucleofilicity of the ring. For example, it is much more difficult to nitrate or chlorinate pyridine, than benzene. It is especially striking in case of 5-membered electron-deficient heterocycles (EDH) with 2 or (better) more heteroatoms, at least one of them being pyridine nitrogen. Examples of these systems are triazoles, oxadiazoles and thiadiazoles. Azo dyes prepared from many heterocyclic diazonium salts have significant batochromic shifts vs. their aromatic counterparts, indicating strong electron-withdrawing properties of heterocyclic ring[2]. This electron deficiency should translate in high reactivity of corresponding diazonium ions.

Another potential advantage of heterocyclic amines as treating agents may be the fact that, contrary to benzenoid compounds, heterocycles are usually assembled from relatively simple [3+2] or [4+1] fragments, providing large number of possibilities. It has to be noted, however, that the cyclization procedures often involve aggressive condensing agents ($POCl_3$, $SOCl_2$, strong acids etc.), limiting useful synthetic opportunities. For industrial application, such as InkJet ink or Toner components, the price also plays a very important role.

A very good example of diazo-EDH high reactivity is given in an article by Haubrich and Goerdeler[3].



I

Heterocycle (Het)		Yield %
	(PABA)	0
		0
		25
		52
		85
		95 (20% with m-xylene)

Diazotized anilines are not reactive enough to couple with mesitilene (I). Authors clearly demonstrate that 5-membered heterocycles with 3-4 ring heteroatoms have considerably increased reactivity, so coupling with mesitilene and even with less reactive m-xylene becomes possible and proceed with reasonable yields.

Design and Selection of Molecules

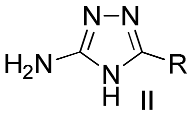
In order to obtain a useful and practical solution for InkJet application the new treating agent should meet a few criteria:

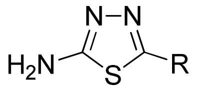
1. It should be diazotizeable, which is not necessarily true for any heterocyclic amine – many of them react with nitrous acid and its equivalents just to generate corresponding nitroso derivatives. In some cases

diazotization leads to complete degradation of the molecule[4].

2. The second function, attached to the ring is the group, needed for application properties, i.e. it should be a cationic or anionic group, a hydrophobic group, a group to link to the polymer and the like. With a 5-membered heterocycle, having 3 heteroatoms, this leaves just one position for such a group, whereas heterocycles with 2 heteroatoms allow for two groups to be attached. Unfortunately, imidazole and thiazole diazonium compounds are not much more reactive than corresponding benzenoid compounds. From steric considerations, it is needed, that amino group and the functional groups should not be in ortho position to each other.
3. A feasible synthetic route(s) or commercial availability of the compound is of extreme importance for industrial application.

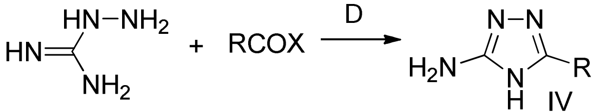
These requirements focused this study on two classes of heterocyclic amines – 2-amino-1,3,4-1H-triazoles (II) and 2-amino-1,3,4-thiadiazoles (III).


II

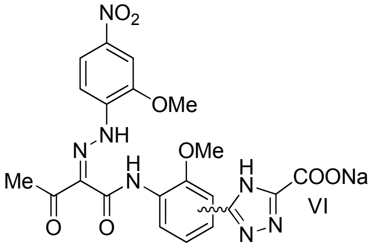

III

It should be noted here, that although pyridines, pyrimidines, and *s*-thiazines are also electron-deficient cyclic systems, many of their amino derivatives do not diazotize properly[4], and if they do, synthetically the needed molecules provide much higher challenge than triazoles and/or thiadiazoles.

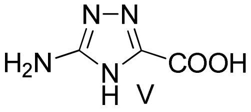
Aminotriazoles - Synthesis

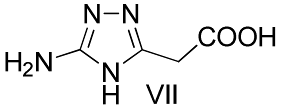

X = OH, OEt, Cl, etc.

Classic synthesis of aminotriazoles (IV) uses inexpensive aminoguanidine (which in turn is generated from cyanamide and hydrazine) and derivatives of carboxylic acids[5]. Reaction does not require an organic solvent and usually proceed with very good yields. There are dozens of references dedicated to this synthesis; many aminotriazoles are available. Aminotriazolecarboxylic acid (V) is manufactured by several producers. It can be diazotized and we used it as a treating agent for Carbon Black or color pigments, such as PB15:4, PR122 or PY74. In the case of PY74, a relatively inert azopigment, we were able to demonstrate that diazotized V is much more reactive than traditional diazo treating agents, leading to higher treatment level and improved stability. Formation of the treatment product (VI) was demonstrated by LC-UV-MS[6].


VI

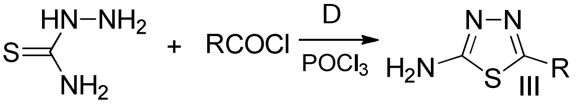
Another easily obtainable triazole is the aminotriazoleacetic acid[7] (VII). It is remarkable, that the diazonium ion, derived from VII is much less reactive towards pigments, than the one generated from V.


V

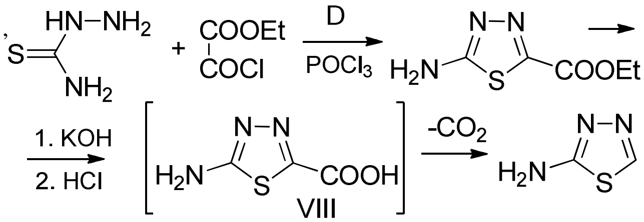

VII

Aminothiadiazoles - Synthesis

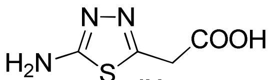
Similarly to II, there are quite a few syntheses of III. They are often based on [4+1] cyclization of acid chlorides with thiosemicarbazide[8]. In this case however, use of strong condensing agent, such as PCl_3, $POCl_3$ or $SOCl_2$ is required, which brings certain restrictions on the functional groups introduced.

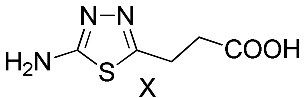


A typical and most convenient ionizeable group to be attached to III is a carboxy group. Interestingly, thiadiazole cycle is much more electron-deficient, than a triazole, so the carboxy group should be 'insulated' from the ring. Of the three compounds (VIII-X), compound VIII cannot be prepared, as it quickly and completely decarboxylates at room temperature:



Compound IX, when converted to diazonium salt, degrades, and only aminoacid X is stable and can be used.


IX


X

Compound X turned out to be a very versatile and aggressive treating agent, effectively grafting a (β-carboxyethyl)thiadiazolyl residue onto the surfaces of Carbon Black and color pigments.

Preparation of Pigment Dispersions

All surface treatments of pigments were done at room or slightly elevated temperature, by mixing the pigment, water and sulfiuric or methanesulfonic acid and slowly metering in sodium nitrite solution. Diazonium reaction was followed by the standard work-up described in our other publications[9]. The solids content of all dispersions after final purification was around 15%; viscosity - usually close to 2 cps. All dispersions were stable in prolonged (up to 8 weeks) heat aging tests (as dispersions and in typical ink formulations). Some properties of dispersions with a sodium counterion are presented in the Table 1 (sodium content on dry basis). All dispersions were formulated into inkjet inks and a number of printing tests had been conducted, using both piezo and thermal printing devices (HP Multipurpose Paper, 4% pigment loading and 100% duty cycle). No firing issues were observed.

Table 1 – Obtained Dispersions

Pigment	Treating Agent	Particle size, nm	Sodium, p.p.m.
Carbon Black	V	141.1	10,879
PB15:4	V	114.1	7,784
PR122	V	127.6	5,084
PY74	V	189.9	3,559
Carbon Black	X	130.3	5,302
PB15:4	X	107.2	4,353
PR122	X	104.6	3,600
PY74	X	197.8	2,090

Some of the printing results for dispersions, generated using thiadiazole treating agent X, are presented in Table 2. The print density is indicated as O.D. for black and as chromaticity for cyan, magenta or yellow.

Table 2 – Print Data –Treatments by Thiadiazole X

Dispersion	OD	Chroma
Carbon Black	1.40	n/a
PB15:4	n/a	44.0
PR122	n/a	56.5
PY74	n/a	72.9

Summary

Certain diazonium salts, containing a 5-membered heteroaromatic ring exhibit enhanced activity in modifying pigments, thereby resulting in modified pigments with a high treatment level and good dispersibility in an ink composition. The structure of the treating agent, specifically the heterocycle itself and the ionizeable (dispersing) group needs to be carefully designed to meet application requirements. Such diazonium salts, due to their high reactivity, can also be used to effectively modify pigments that might not otherwise be modifiable.

References

[1] Cabot Corporation, internal reports.
[2] A.D. Towns, *Dyes and Pigments*, **42**, 3-28, (1999)
[3] J. Goerdeler, H. Haubrich, *Chem. Ber.,* **93**, 397-405, (1960)
[4] R.N. Butler, *Chem. Rev*., **75**(2), 241-257, (1975)
[5] M.R. Atkinson, A.A. Komzak, E.E. Parkes, J.B. Polya, J. Chem. Soc., (1954), 4508-4511.
[6] Cabot Corporation, internal reports.
[7] V.M. Chernyshev, A.V. Chernysheva, V.A. Taranushich, *Russian Journal of Applied Chemistry*, **82**(2), 276-281, (2009).
[8] J.H. Clark, J.P. English *et al*., *J. Am. Chem. Soc*, **68**(1), 96, (1946).
[9] A.I. Shakhnovich, Application WO 2007 102,500.

Author Biography

Alex Shakhnovich received his MS in Chemistry in 1972 from Moscow State University and his PhD in Heterocyclic Chemistry (1979) from Institute of Dyes and Intermediates (Moscow, Russia). He had been working in different academic and industrial institutions in Russia and (since 1991) in US, including Clariant and General Electric. Since 2002 he is working at R&D center of Cabot Corporation in Billerica MA. Dr. Shakhnovich holds a position of Cabot Research Fellow in Industrial Organic Chemistry. His research interests include synthesis, surface modification and application of organic colorants.