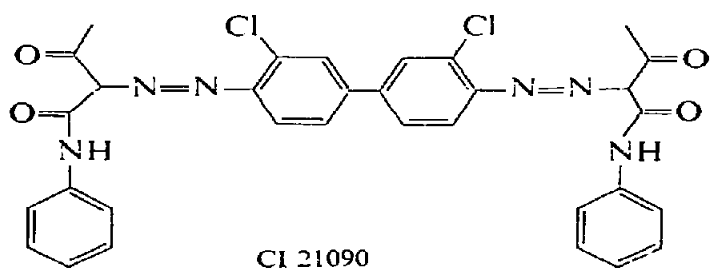
Dyes and Pigments 4 (1983) 321–323

Letter to the Editor

Dear Sir,

We would like to comment on the paper by Matsukawa *et al.*[1] concerning the synthesis of substituted 3,5-bis(*p*-aminophenyl)-*N*-amino-1,2,4-triazoles and the use of those chemicals in the preparation of 'Benzidine Yellow' type pigments. Although the chemistry presented and the properties of the products are most interesting, we are concerned with the casual manner in which one of the products is presented as a direct substitute for 'Benzidine Yellow', as well as the implication that 'Benzidine Yellow' pigments are carcinogenic.

With respect to the terminology used by the authors, the name 'Benzidine Yellow' for the chemical structure shown below is inappropriate.



CI 21090

Although the material is sold under many different trade names, the widely recognized generic name is CI Pigment Yellow 12. Indeed, we know of no pigment that currently uses benzidine as its basic diamine component.

Unfortunately, the confusion in the paper also extends to the prevailing knowledge of the health effects associated with these chemicals. Although benzidine is a human carcinogen and some of its substituted analogues are regarded as experimental carcinogens, the evidence as to the carcinogenicity of benzidine derivatives is not always conclusive.

Pigments based on dichlorobenzidine (DCB) or other substituted diaminobiphenyls have not been found to be carcinogenic. In fact, three independent bioassays on CI Pigment Yellow 12[2-4] show no evidence of carcinogenic activity for this compound. Additionally, several studies[2,5,6] have failed to confirm an earlier publication claiming that a related pigment, CI Pigment Yellow 13, is metabolized to its starting amine, 3,3'-dichlorobenzidine.

Accordingly, we feel that the substitution of pigments based on substituted bisaminobiphenyls is not necessary for toxicological reasons. Whether it is possible and economically feasible, as suggested by the authors, is another question and requires discussion of the application, health and environmental effects, and production capabilities and costs associated with each pigment.

With respect to the application of different pigments, it is unlikely that a pigment will be found which is so similar in its major properties to another that it may be used as a direct substitute. Some property such as color, strength, opacity, refractive index, particle size, etc., is sure to be so different that reformulation by the user is usually necessary in order to substitute effectively one pigment for another.

As to health and environmental effects, we have already pointed out that the CI Pigment Yellow 12 for which the authors offer substitutes is not carcinogenic. We find, however, no indication in their paper that they have conducted long or short term toxicity tests with their triazole-based pigments. We acknowledge that an earlier publication of one of the authors demonstrates (through limited experiments) that 3,5-bis(*p*-aminophenyl)-1,2,4-triazole has much less toxic or carcinogenic activity than benzidine. We note, however, that this chemical is only one of the materials used in the synthesis of the substitute pigment. Other precursors to the substitute pigment with carcinogenic or mutagenic potential are hydrazine (experimental carcinogen), 4-bromo-2-methyl benzene amine (mutagen) and mercaptoethanol (mutagen). Cuprous cyanide (acute toxicity, fish toxicity) and dimethylformamide (acute toxicity) are also of concern. Possible releases to the environment and exposure to these chemicals during precursor and pigment manufacture have to be considered. We are sure that with proper safety engineering, exposure can be kept to a minimum, but the same already holds true for dichlorobenzidine. For DCB, strict OSHA standards have been in place in the United States since 1974, even though a large body of epidemiological work on DCB exposure has shown no adverse health effects in humans.

Finally, we note that production facilities for the described chemistry in the volume range of 10 000 metric tons of pigment per annum simply do not exist. Technical development and plant construction would take anywhere between three and five years and would increase the cost of the substitute pigment significantly. The chemistry used in the synthesis of triazole-derived pigments may result in additional costs as compared to the CI Pigment Yellow 12. In the first pigment synthesis, the comparable starting materials are substituted bis-phenylamino-triazoles as opposed to dichlorobenzidine. The latter is made from *o*-chloro-nitrobenzene in a two-step process with an overall yield of better than 70 %. By comparison, the reported yield of the two-step process from 2,6-dichloro-4-bromo-aniline to the corresponding triazole compound is no better than 49 %. We further note that the cost for the brominated dichloroaniline may already be as high as that for dichlorobenzidine. It follows that the cost of the final triazole compound cannot be anywhere near that of dichloro-benzidine. The cost for the resulting pigment substitute thus would be prohibitive for the typical pigment user.

In conclusion, we believe that the authors have presented interesting research. Their findings, although not sufficient to show that pigments based on bis(*p*-aminophenyl)-triazoles are viable substitutes for CI Pigment Yellow 12, have displayed some of the complex requirements associated with the substitution of chemical products with others believed to be less hazardous.

REFERENCES

1. K. Matsukawa, J. Setsune, K. Takagi and T. Kitao, *Dyes and Pigments*, **3**, 307 (1982).
2. F. Leuschner, *Toxicology Letters*, **2**, 253 (1978).
3. *Bioassay of Diarylide Yellow*, NCI-DHEW Publication No. (NIH) 77-830.
4. ICI, *PX Monolite Yellow GTS: Carcinogenic Study in the Rat*.
5. C. Nony, National Center for Toxicological Research, NCTR Technical Report for Experiment No. 196, March 1979.
6. A. Mondino *et al.*, *La Medicina del Lavoro*, **69**, 693 (1978).

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