Color By Design Before 1890

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"The time of the 'Arcanists' is over. Whosoever, in the last quarter of the nineteenth century, will give his colleagues a chemical puzzle must be prepared to see it solved sooner or later." (*1*). With these words, published during 1877 in the journal of the German Chemical Society, the academic chemist August Wilhelm Hofmann admonished the industrial chemist Otto N. Witt, who was angered by Hofmann's publication of the chemical constitution of a commercially successful new azo dye.

For a short time the nature of this dye, chrysoidine, had been a well kept secret, shared by its discoverer, Witt, on behalf of his English employer, by Heinrich Caro, the BASF technical director, and by Peter Griess, the pioneer of azo dye chemistry. Two years earlier, in 1875, Hofmann had revealed the structure of another new dye, eosin, and "thus disclosed to all the world an important manufacturing secret." Until 1877, protection of chemical discoveries by keeping them secret, a legacy from the times when dye recipes were kept within the family, was often considered the best way of protecting inventions in the synthetic dyes industry, especially in Germany. This was hardly surprising considering the different systems for granting legal monopoly that existed in the various German states, and the lack of understanding of new chemical processes by patent examiners.

However, in 1877 a new German patent law came into force which gave comprehensive protection over all the territories of the new Reich. This immediately modernized the style of dye innovation, and imposed a greater reliance on scientific studies. Competitive activity now required academic and industrial collaboration, and improvements in industrial research. Chemists were encouraged to embark on novel dye making campaigns; and the industrial dye making concerns were encouraged to rely on the law of patent monopoly as a means of protecting useful discoveries. The effect was dramatic: patent activity mushroomed, the rainbow of commercial dyes proliferated, and chemical knowledge was applied with confidence to even greater conquests, like synthetic indigo. The age of colored molecules designed in the laboratory had arrived.

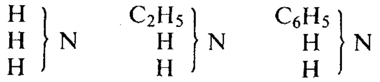
August Wilhelm Hofmann was at the center of many chemical investigations of synthetic dyes between 1860 and 1880.

This paper concerns the prelude to this era, especially the first attempts to rationalize what we might legitimately call color by design in the early 1860s. Hofmann's early work with aniline red and its derivatives will be the main focus, and this includes some background discussion on contemporary ideas about chemical formulae. Azo and anthraquinone dyes also play prominent roles in the story, and were essential to Witt when he developed a successful theory of color in 1876, but treatments of their structures are less rigorous, since the former have been covered by David H. Wilcox Jr. (*1*) and in an account of alizarin (*2*).

Hofmann and the Ammonia Type

The road to the remarkable achievements of the dye industry at the end of the nineteenth century encountered numerous potholes, providing challenges and puzzles for academics and industrialists alike. Dye makers were confronted with problems of making, predicting and designing colors right from the moment that the first synthetic dyes—aniline purple (mauve) and aniline red (fuchsine, or magenta)—became commercial successes in the spring and summer seasons of 1859. Fortunately, even then science based industrial enterprise progressed hand in hand with the development of classical organic chemistry, and the search for knowledge about the relationship between color and chemical constitution commanded the attention of many leading chemists, most notably A.W. Hofmann.

Hofmann's most important early investigations lasted from around 1861 to 1865, before the announcement of Friedrich August Kekulé's benzene ring theory. During that time the most popular way of expressing chemical constitution was through the type formulae, a system of classification which placed chemical compounds in groups according to their relationships to a simple parent substance, like water or ammonia. These formulae indicated the rational composition, showing which particular groupings of atoms replaced hydrogen in the parent. The Liebig trained Hofmann, director of the Royal College of Chemistry in London, refined the ammonia type, of which aniline and ethylamine were important members.



$$\left.\begin{matrix}H\\H\\H\end{matrix}\right\}N \qquad \left.\begin{matrix}C_2H_5\\H\\H\end{matrix}\right\}N \qquad \left.\begin{matrix}C_6H_5\\H\\H\end{matrix}\right\}N$$

ammonia ethylamine aniline

Type formulae were not structural formulae; they simply showed the atomic groupings present as hydrogen atoms were replaced by other atoms or "radicals."

Hofmann expended considerable effort towards assigning the complex aniline colors to the ammonia type. Although these compounds could not be made to fit, this work paid many dividends and drove forward research that resolved commercial problems, produced new products, and, at the same time, enhanced the status of chemistry.

Production of aniline red was based on cooking commercial aniline with various oxidizing agents in efforts to increase the yield and to circumvent patented processes. From 1860, the most popular oxidant was arsenic acid. Aniline blue, discovered early in 1860, was an accidental coproduct of the arsenic acid process, obtained when too much aniline was present, and this new dye was the basis of immediate chemical studies. At this stage the design of colored molecules meant simply using science based empirical methods, and gathering information about reagents and products in attempts to write formulae, to fit products into classes, and to draw equations.

The First Stage Towards Design: Methods, Formulae and Equations

Before the benzene ring was available, the aromatic compounds aniline red and blue were known to contain carbon and hydrogen, thought to be present in some dense, intimate union, as well as nitrogen. Chemists considered that aniline red was an oxidation product; some claimed that it contained other elements like oxygen or chlorine. Hofmann confirmed that aniline red was formed from three molecules of aniline; the free base of the red he called rosaniline. He noted that reduction destroyed the color, which was restored upon subsequent oxidation. It was anticipated that certain hydrogen atoms in the red might be replaced by other atoms or groups to produce new colors.

No suitable theory was available to enable chemists to work out the structures of dyes, their coproducts and derivatives. Hofmann, although greatly intrigued by the variety of nitrogen compounds found during large scale production of intermediates and dyes, could not express them by his cherished ammonia type: "The theory which (in 1852) satisfactorily represented the constitution of the nitrogen bases then examined, requires an expansion to include the tinctorial ammonias added to our knowledge during the last decade. The time for the enunciation of this amplified theory has not yet arrived."

Industrial progress in organic chemistry was taking place at a far greater pace than theoretical and laboratory progress, and Hofmann, who was at the center of collaborative studies involving industry and science, had to admit in December 1862 that: "Though proud of her office as guide of industry, science acknowledges without blushing that there are territories on which she cannot advance without leaning on the strong arm of her powerful companion. Joint labours of this kind cannot fail to seal the pledge of alliance between industry and science." (*3*).

However, within six months he was in a position to report his first success. "The prosecution of my researches on the aniline colours has led me to a result of great simplicity. . ." He had shown, by careful analysis and characterization, that aniline blue was phenylated rosaniline, an exciting scientific discovery, one that would interest many chemists and industrialists in European centers. Hofmann immediately transmitted news of this discovery to Paris by telegraph on 18 May 1863, where it was announced at the termination of that day's sitting of the *Académie des Sciences.* A communication was received by the Royal Society in London on 21 May, just in time for publication in the *Proceedings* of that date (*4*).

Magenta and Aniline Blue

At first it was assumed that the coal tar dyes were formed from aniline alone. Hofmann found otherwise. With pure aniline extracted from indigo, he showed that the base did not give aniline red when treated with the most popular industrial oxidants. Aniline from other sources gave the same negative result. A London manufacturer, Edward Chambers Nicholson, "who combines the genius of a manufacturer with the habits of a scientific inquirer," informed Hofmann that he had long known of the inability of pure aniline to produce aniline red.

To resolve this mystery Hofmann examined samples of aniline used in the industrial processes. These all gave aniline red under the usual conditions, but their boiling points were found to be higher than that of pure aniline, leading Hofmann to conclude that another reactant was present. New experiments were required (*5*). The results were just as outstanding as his discovery of the nature of aniline blue. "A mixture of pure aniline and pure toluidine, when heated with mercuric chloride, stannic chloride, or with arsenic acid," Hofmann reported, "instantaneously produced a magnificent red of most intense tinctorial power." He thereby proved that aniline alone could not produce the red color, but required the presence of toluidine. This helped explain the formula of aniline red, and was the starting point for reinvestigation of the blue.

Friedrich August Kekulé, whose benzene ring theory transformed the understanding of color and constitution after 1865.

In his research into the blue, Hofmann once more made use of observations communicated from industrial chemists. The evolution of ammonia as aniline red turned to aniline blue was significant. Hofmann's usual precise analysis gave the formula $C_{38}H_{32}N_3\,Cl$ for the hydrochlorate of the blue, which showed that three phenyl groups had made their way into aniline red. This made it possible to write an equation for the formation of aniline blue:

$$\begin{array}{ll} C_{20}H_{19}N_3,HCl + 3C_6H_7N = & \\ \text{rosaniline salt} + \text{aniline} = & \\ C_{20}H_{16}(C_6H_5)_3N_3,HCl + 3H_3N & \\ \text{aniline blue} \qquad + \text{ammonia} & \end{array}$$

The color change on substitution prompted Hofmann to note: "A lively imagination might feel tempted to speculate on the relation between color and composition; but there are other questions claiming more immediately the attention of the experimentalist." (*6*).

Hofmann's further interest came from the more general phenomenon of phenylation, which he had earlier attempted without success by the reaction between aniline and phenol. The purpose of this was to replace one or both hydrogen atoms of the amino group in aniline by the much larger phenyl group. It was surprising to him that the phenyl group could be introduced into magenta but not into the much smaller molecule of aniline. "Diphenylamine and triphenylamine are substances existing at present only in the conception of the chemist. It was reserved for the peculiar, I might almost say instinctive mode of experimenting belonging to industry to fill up this blank."

Hofmann was particularly puzzled by the nature of phenylation of aniline red. Did it occur on replacement of hydrogen atoms by the phenyl group, or on insertion of aniline into aniline red after it had released ammonia? The answer was not to be revealed for some time, but the question pointed towards investigation of the corresponding alkylation reaction. This was stimulated by an 1861 publication of the French chemist Emile Kopp, an expert in madder colors, and consultant for a dye manufacturer involved in a major patent dispute. Kopp believed that aniline red was a triamine in which one hydrogen atom had been replaced by a nitro group. This was incorrect, but, happily, it led to useful speculation: a whole range of colors might be obtained by similar replacement reactions, in which Kopp named the halogen derivatives as possible new reds, and alkylated derivatives as the basis of other colors (*7*).

Hofmann's first successful trials were made with ethyl iodide acting on the red, the product of which "dissolves with a magnificent blue color in alcohol." Advertising his discovery, Hofmann stated that the "tinctorial powers of this solution are scarcely inferior to that of rosaniline itself; and industry will probably not disdain to utilize this indication of science." Apart from the theoretical questions, Hofmann had now made his own contribution to the range of aniline colors with his aniline violet, that was duly patented and licensed to British, German and French dye makers.

With all this information in hand, Hofmann was encouraged to reflect on whether replacements of groups other than phenyl and alkyl might produce an even greater range of colors. He asked, "Whether the substitution for hydrogen in rosaniline of radicals other than methyl, ethyl and amyl, may not possibly give rise to colors differing from blue; and whether chemistry may not ultimately teach us systematically to build up colouring molecules, the particular tint of which we may predict with the same certainty with which we at present anticipate the boiling point and other physical properties of the compounds of our theoretical conceptions?" This was the first concrete statement concerning the design of colored molecules based upon a good scientific foundation.

Classification of Aniline Dyes

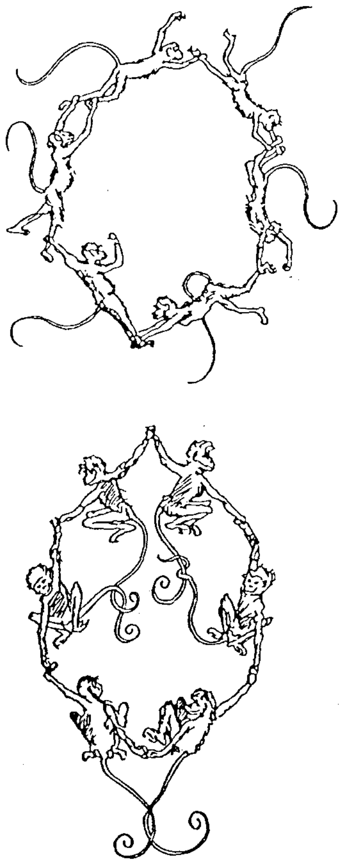
Following a disagreement with the German chemist Hugo Schiff over the formula of aniline blue, Hofmann stepped up his efforts aimed at determining the "atomic construction" of both the violet and blue derivatives of rosaniline. The most far-reaching discoveries were the substituted anilines which resulted from degradative distillation. From commercial Hofmann's violet he obtained ethylated aniline (ethylaniline). From basic oils distilled out of aniline blue he obtained the previously unobtainable diphenylamine, expressed according to the ammonia type formula, as:

$$\left.\begin{array}{c} C_6H_5 \\ C_6H_5 \\ H \end{array}\right\} N$$

(diphenylamine = phenylaniline) (*8*).

The recovery of these and similar compounds provided information concerning the manner of substitution in aniline red compounds (*9*). They showed that the substitution reactions, in which blue and violet were formed from red, had taken place by displacement of amino group hydrogens in the red and not by displacement of phenyl group or methyl group hydrogens.

The degradation products of aniline red (rosaniline) and its derivatives are shown below. The release of aniline and of its respective substituted derivatives showed that hydrogen atoms in amino groups had been displaced in the formation of blue and violet compounds.



Cartoon of the benzene ring, in which monkeys replace carbon atoms.

aniline red $\longrightarrow$ aniline + ammonia
(rosaniline)
aniline blue $\longrightarrow$ diphenylamine
toluidine blue $\longrightarrow$ phenyltolylamine
aniline violet $\longrightarrow$ ethylaniline

The Equation for Aniline Red

A further response from Hofmann to his critics concerned the equation for the formation of aniline red. He had commented that Schiff's equations "are not conspicuous for elegance and simplicity," and felt that the equation:

$$\underset{\text{aniline}}{C_6H_7N} + \underset{\text{toluidine}}{2C_7H_9N} = \underset{\text{aniline red}}{C_{20}H_{19}N_3} + 6H$$

"might be looked upon as an expression closely approaching truth." Although nothing was known about the isomers of toluene, and even less concerning the various isomers and homologues of the red dye, this equation performed a useful function in that it became a useful guiding tool for both theoretical and practical studies.

Hofmann's final word on the structure of aniline colors was embodied in his modified ammonia type, the three-fold ammonia type:

$$\left.\begin{array}{l} (C_6H_4) \\ (C_7H_6)_2 \\ H_3 \end{array}\right\} N_3, H_2O$$

aniline red

$$\left.\begin{array}{l} (C_6H_4) \\ (C_7H_6)_2 \\ (C_6H_5)_3 \end{array}\right\} N_3, H_2O$$

aniline blue

$$\left.\begin{array}{l} (C_6H_4) \\ (C_7H_6)_2 \\ (C_2H_5)_3 \end{array}\right\} N_3, H_2O$$

aniline violet

Hofmann ended with a wise word of caution. "We must not, however, forget that this is simply an hypothesis."

In his laboratory work, Hofmann had tried the reaction of aniline red with nitrous acid, the diazotation reaction, the chemistry of which was uncertain. He did not succeed, but this reaction was later used to determine the correct structure of aniline red and of its derivatives. The red was converted to rosolic acid, a phenol derived synthetic dye. This relationship between the red base and the corresponding hydroxy compound, noted in the mid-1860s by Heinrich Caro and Alfred Wanklyn, who proposed an ethylene type formula for the red, was used in the 1870s by Emil and Otto Fischer in Strasbourg. They followed the observation of the Manchester dye manufacturer Richard Dale (whose father had made Caro a partner in their business) and one of his consultants, Carl Schorlemmer, who achieved the reverse and produced an aniline red from its corresponding trihydroxy compound. The Fischers showed that the red was a compound based on the structural unit of methane, that is, it was a triphenylmethane compound, formed by condensation of three molecules of aniline and its homologues. Pararosaniline was the most common derivative. Hofmann's obsession with his ammonia type probably caused him to overlook the possibility of using the methane type as a means of expressing aniline dye formulae in the 1860s.

The Patent Cases and The Design of New Colors

Before 1865 there were a number of important patent cases involving British and French firms. In France, one manufacturer, Renard Fréres of Lyon, gained control of all the processes for aniline red and blue. Although in Britain the red process became public property, the blue patent, belonging to the same French concern, was available only to the licensees. In both Britain and France the results of the aniline dye patent cases encouraged innovative activity in attempts to circumvent patent rights.

A new blue dye was soon made by a

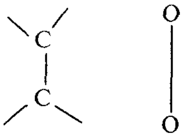
process which used a different starting material, aniline in which hydrogens of the amino group were replaced by phenyl groups (*N*-arylation). The same method was used to obtain violets, starting with aniline in which hydrogens were replaced by alkyl groups, such as methyl. Charles Lauth had achieved laboratory alkylation of aniline in 1861, but it took until 1866 before *N*-substitutions were available in industry. The processes were dangerous, requiring high pressures, and there were several fatal accidents.

It was not realized that these new products were essentially the same as those obtained by substitutions on aniline red. Although Hofmann had suggested that they were identical, Heinrich Caro, Carl Graebe and others later disputed this, and the controversy lasted over two decades. Nevertheless, from a practical point of view this was an important step forward in the design process, and made available methods for a range of *N*-substituted intermediates for later generations of dyes.

The Benzene Ring and the Structures of Anthraquinones

The major breakthrough in the chemical understanding of the new styles of dye making came after Kekulé put forward his theory of the benzene ring to explain the unique nature of aromatic hydrocarbons. He saw the ring as a closed chain of six carbon atoms, expressed as C_6A_6, where A is, in modern terminology, the valency. According to this formula, the six free valencies can each join up with an atom or group which has a valency of one. If six hydrogens are involved, the formula C_6H_6 represents benzene.

There were many questions to be resolved before the theory gained widespread acceptance. Two of the loose ends were larger aromatic systems, like naphthalene and anthracene, and the diketone compound known as quinone; all were to become important to dye chemistry. These particular puzzles were sorted out by Carl Graebe and Carl Liebermann, assistants of Adolf Baeyer at the Gewerbe Akademie, Berlin, when they established that alizarin was an anthraquinone. Soon after, the synthesis of alizarin was achieved from the coal tar hydrocarbon anthracene, and the dye industry entered a new era, based on the replication of nature's molecules, and theory induced research. Inspired by their own success with alizarin, Graebe and Liebermann in 1868 put forward a theory of colored molecules based on the azo group (−N=N−) and on the quinonoid structure, which they drew as a closed ring:



They emphasized the importance of unsaturation in producing color, and that reduction of colored substances, like quinone, azobenzene and nitro compounds, caused loss of color. This was perhaps their most significant contribution, especially as they were hampered by insufficient structural information, which caused them to assign the small ring arrangement to the quinone group, and an angular structure to anthraquinone.

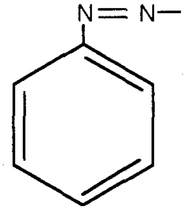
Kekulé's benzene ring encouraged a vast experimental effort that provided rules for the location of substituents, and enabled good structural approximations of many aromatic molecules. This was aided by degradation to parent hydrocarbons, precise elemental analysis, and knowledge of characteristic reactions of the functional groups. Synthetic studies provided confirmations and corrections.

The linear structure for anthracene, and thus of anthraquinone, became available in the early 1870s, and this enabled Adolf Baeyer and Heinrich Caro (who had joined BASF in 1868) to work out the modern structure of alizarin in 1874. They exploited the new phthalein reaction, the condensation of phthalic anhydride with phenols, the basis of xanthene dyes. Baeyer also used this general reaction to condense resorcinol with phthalic anhydride to afford fluorescein. Caro brominated this product to obtain the highly successful dye eosin. Since more dye structures were now available, common features of their architectures could be established, and predictions made. This brought theory based design of colored molecules closer to the reach of chemists.

The Development of Azo Dyes

To many people, the most enduring image of Kekulé's benzene ring is the cartoon in which monkeys appear in place of carbon atoms. This appeared in a hoax pamphlet put out by two of Kekulé's young disciples. One of them was Otto Witt, the Swiss-trained chemist who in 1875 was working for a dye making company at Brentford, near London. He investigated the diazo reaction, known since 1858 when it was discovered by Peter Greiss, and which gave strongly colored azo products insoluble in water.

The constitution of the azo compounds presented many problems to chemists. Griess and others thought that the two nitrogen atoms of the azo grouping had actually entered into benzene by replacing two hydrogen atoms. In 1866 Kekulé published a structure suggested by his work on the ring theory. This was the phenylazo radical (the modern phenyldiazonium ion):



The azo compound structure was completed by attaching a second group (X) to the vacant end of the moiety, −N=N−.

However, and despite their promise, no successful examples of the azo dyes were brought to market during the next decade. This situation changed in 1875, at a time when Witt was working on an improved theory that related color to structure. He searched for an unknown azo dye containing two free amino groups, believed to be the missing link in a series that included a yellow and a brown dye.

Witt's Series	Properties
aminoazobenzene	Yellow, fugitive
diaminoazobenzene	?
triaminoazobenzene	Brown, fast

Witt predicted that the missing dye was an orange color, and also that this would be of moderate stability. He was drawn to the work of Baeyer and Jäger who had just published an important paper suggesting the notion of coupling in the azo reaction, that is, the terminal nitrogen of a diazonium ion attaches itself to another aromatic system. This caused Witt to discover the missing dye, with the expected properties, and it was successfully marketed as chrysoidine. Witt shared details of his process with Caro and Griess, and they agreed that the information should be kept secret. The pharmacist Roussin determined a similar general route to azo dyes, taken up by Poirrier in Paris.

Carl A. Martius, a partner in the Agfa firm of Berlin, brought a sample of the new chrysoidine dye and gave it to his consultant, Hofmann, now in Berlin, who quickly published the formula. The chrysoidine reaction became public property, and numerous firms throughout Europe exploited the process, to the great disappointment of Witt and Caro. In Germany, this type of situation disappeared with the enactment of the patent law; chemists could protect their new azo and other dyes, and this, in turn, encouraged better organized research activities.

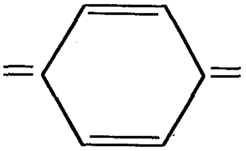
Chemists became engaged in exploiting the azo reaction to produce compounds of the form $\mathrm{Y{-}N{=}N{-}X}$, in which different combinations of X and Y were introduced. This involved thousands of experiments, most of which gave colored compounds that were of no use as dyes. Nevertheless, a degree of theory based design of colors was possible. For azo dyes, wide ranging structural variations relied on the availability of intermediates created in over thirty years of intensive efforts. Witt, for example, added resorcinol to the diazonium salt to afford the orange dye tropaeline O. Other azo dyes were made from naphthalene and *N*-substituted derivatives, and the sulphonic acid grouping was introduced into intermediates. When toluene was used instead of benzene, redder shades were obtained.

Witt's Theory of Color and Constitution

Although Hofmann, Graebe and Liebermann considered the possibilities of developing theories about color and molecular structure, the first successful theory on these lines was put forward by Witt in 1876. His familiarity with azo dyes, and improved knowledge of structures that were available in the mid-1870s, enabled him to prepare a theory which showed that two types of functional groups are present in highly colored molecules suited to dyeing. By specifying the nature of these groups, it was possible to narrow down the range of compounds used to create dyes.

This theory concerned the known groupings of chemical elements that appeared to be necessary for the quite separate and specific properties of color and dyeing. Witt had pointed out that all colored compounds must contain in the main structure of the molecule certain arrangements of atoms, such as the azo group, the pair of carbonyls in anthraquinone, or the nitro group, which he called chromophores (Greek *chroma* color; *phores*, from *pherein* to bear). They all contained double bonds. Witt referred to the combination of chromophore and aromatic system as the chromogen. This part of the molecule was colored, but not a dye. The simpler chromogens were restricted to the yellow and orange range. For dyeing, salt forming groups had to be present. For example, azobenzene contained only the chromophore grouping (the azo group), and was not a dye, while its amino derivative, which formed salts, was a dye. Also, removal of salt forming properties by blocking, through, for example, acetylation of amino (NH_2) groups or methylation of hydroxyl (OH) groups, destroyed the dye fixing property (*10*).

Increase of dyeing power followed an enlargement in the number of salt forming groups, and, other things being equal, dyeing power also increased with increase in molecular weight. Later, in 1888, Witt used the term auxochrome for the salt forming groups (Greek *auxin* to increase), and this term came to be associated with substituents responsible for both dyeing and modifying color. Auxochromes deepened color and moved it toward the blue end of the spectrum. There were several refinements of Witt's original theory including Henry E. Armstrong's quinonoid theory of 1888. Armstrong emphasized the role of "incompletely saturated affinities," and intimate associations of atoms, in the expression of color, in other words, multiple double bonds. He adopted Fittig's correct diketone (1,4-) formula for anthraquinone and the quinones, and redrew the structures of magenta, azo, phthalein, and other dyes in such a way that they contained a common component analogous to quinone, that is the structural unit



Although newer theories, available from the early 1900s, suggested that the entire conjugated system was responsible for color, Witt's original concepts remained valid. They have also been carried over into modern theories concerning the nature, number and location of substituents, and are used to introduce ideas about the electronic nature of chemical bonding and electronic transitions in colored molecules. The roots of modern efforts to create and understand color are indeed deeply ingrained in the pioneering work undertaken over a century ago.

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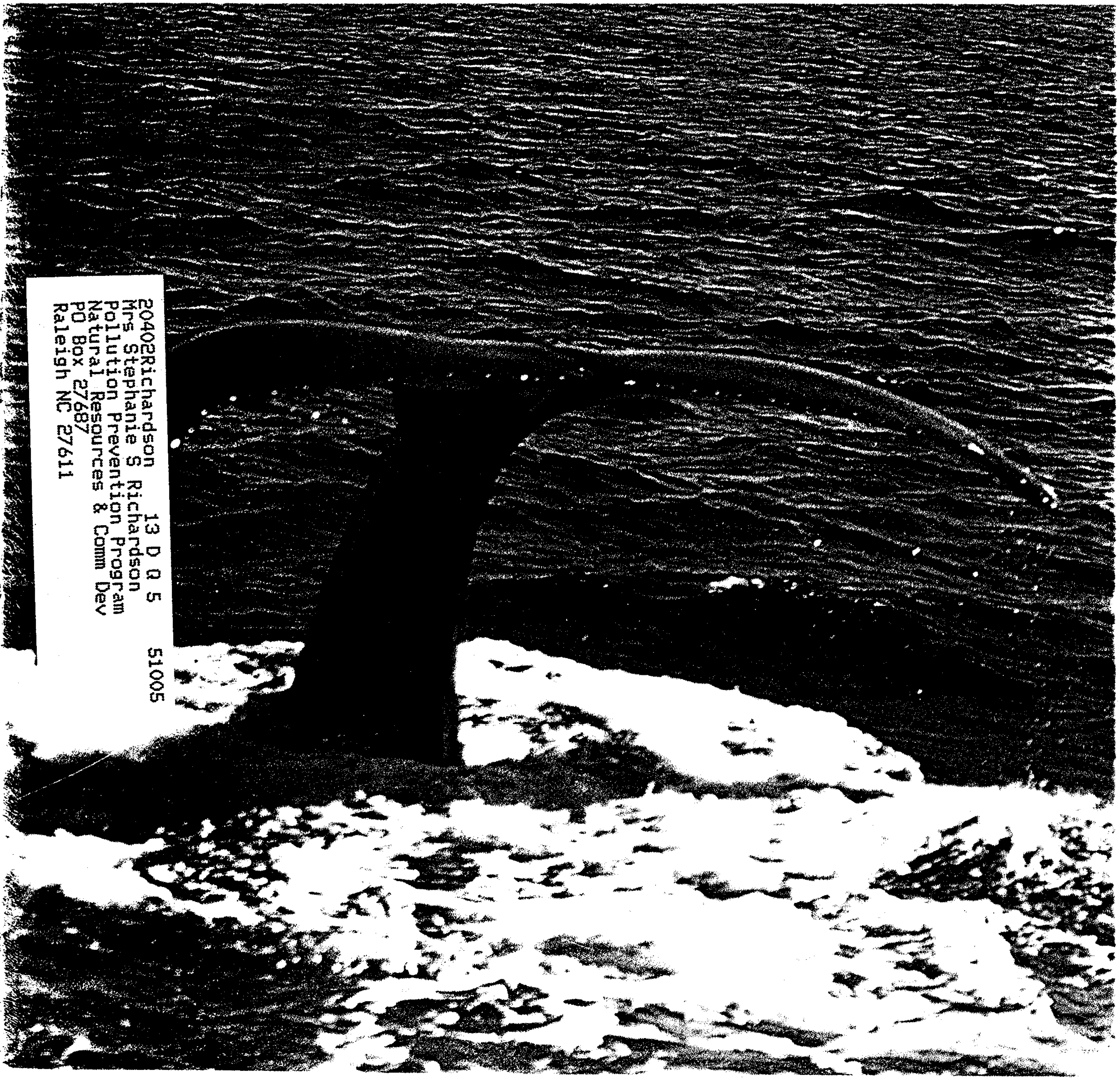

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