Restaurator 12:131-136 C 1991 Munksgaard. Copenhagen

Classical Methods of Bleaching in the Restoration Workshop: The Role of the OH Radical

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INTRODUCTION

Bleaching processes for papers and textiles have been extensively discussed in the restoration literature on the basis of empirical experience.[1] Because of the huge amount of literature and the lack of knowledge on the condition, complexity and history of the bleached objects, a general judgement is quite difficult. There are simple pragmatic reasons to exclude the use of certain bleaching agents in the restoration workshop because the restoration workshop is not a chemical laboratory. Ozone and chlorine dioxide are poisonous and explosive gases that may be handled safely in routine industrial processes. The security of the machinery and the safety education of the personnel are, in general, not guaranteed in a restoration workshop. The trend to exclude poisonous and burning gases from restoration workshops is demonstrated by the use of insect repellents instead of insecticides in museums and archives.[2] This trend should be supported for safety in the workplace. The use of solutions of hydrogen peroxide and sodium hypochlorite for bleaching is demonstrated in many cases in the scientific literature.[3-10] Although many phenomena have not been explored so far, the understanding of the effect of these compounds on textiles and papers is so firmly grounded that general rules on the use of these bleaching agents can be derived.

An ancient object of art, such as an oil painting on canvas or a hundred-year-old etching, has a much more complex character than a scientific object in the laboratory, such as a simple piece of canvas or paper.

The construction of an object of art is quite complex. It is comprised of many different organic and inorganic compounds. Further, the complex character is demonstrated by the unknown history of the object of art such as the nature, extent and time of climatic changes and mechanical stress. A piece of art cannot be extensively researched before bleaching starts. The use of a certain bleaching process always means a real decision. The optimal point in the bleaching treatment cannot be predicted on the basis of established principles, and, of course, success cannot be guaranteed. During bleaching, not only the decomposition products in the paper are oxidized, but also the cellulose. The mechanism of the oxidation reactions uses different agents of bleaching.

HYPOCHLORITE SOLUTIONS: ACID-BASE EQUILIBRIA, IONS, RADICALS AND CHEMICAL KINETICS

Paper mainly consists of cellulose fibres. Through bleaching in restoration, decomposition products should be destroyed by oxidation as much as possible, but the cellulose fibre should not be attacked. Margaret Hey[3] was the first to point out, based on physicochemical considerations, that avoiding the destruction of cellulose by bleaching with hypochlorite solutions requires maintaining the pH above 9.0. The reason is the increase in concentration of hypochloric acid (HOCl) by a decrease in pH. The equilibrium

$HOCl \leftrightarrow H^- + OCl^-$ Eq. 1A

is shifted to the left with decreasing pH, which means an increasing concentration on H^+ ions.

The resulting changes in oxidation potential of the solution by changing the pH are profoundly discussed in the literature.[11] HOCl and OCl^- are stronger oxidation agents than the oxygen in the air:

$2HOCl \leftrightarrow 2Cl^- + 2H^+ + O_2$ Eq. 2A

The object to be bleached and the bleaching agents are, of course, not in a thermodynamic equilibrium. So it is important to know the rate of the bleaching processes to determine the effectiveness of the bleaching agent and the attack on the cellulose fibre. This is called a kinetically controlled bleaching process.

Epstein & Lewin[4] researched the kinetics: the reaction rate of the oxidation of the cellulose fibres in an aqueous hypochlorite solution. They found the following dependence of the reaction rate of the oxidation reaction.

Reaction rate ~ $(HOCl)^2 \times (ClO^-)^{0.5}$ Eq. 3

The reaction rate is proportional to the concentration of HOCl squared and to the square root of the concentration of OCl^-. A change in the concentration of HOCl influences the reaction rate more than a change in the concentration of OCl^-. If the equilibrium in Eq. 1A is shifted to the left, the rate of the oxidation reaction increases. This is the case if the pH decreases. Close to pH7, the reaction rate is at a maximum.

A piece of art is a complex unity that combines organic and inorganic compounds. So it is of interest how much the reaction rate is influenced by metallic compounds. This was examined by Nevell & Singh.[5] Eq. 3 for the relationship between the reaction rate and the concentrations in HOC1 and $OC1^-$ was confirmed in the response of metallic compounds. Although the absolute reaction rate increases by a factor of 10-20, the kinetics do not change.

This means that the mechanism of the reaction does not change either.

Based on these kinetics, a radical mechanism is derived for the oxidation of cellulose fibres in aqueous solutions of hypochlorite:

$HOCl + OCl^- \rightarrow OH + ClO + Cl^-$	Eq. 4
$OH + OH \rightarrow H_2O + 0.5\ O_2$	Eq. 5A
OH + cellulose → cellulose radical + H_2O	Eq. 6
$HOCl$ + cellulose radical → oxidation products + HCl	Eq. 7A

Besides oxidation products, chloric acid is formed. This means that the pH decreases and the reaction rate increases; close to pH7, a maximum reaction rate is reached. Radical reactions are not very specific. This results from the reactive character of the OH radicals.

For burning processes, such as paper with air, OH radicals are the most important reaction carriers. A combustion process is the complete oxidation of cellulose to water, carbon dioxide and ash. OH radicals are also found in biological systems; here, because of their high reactivity, they are poisonous. If the poisonous effect is not desired, the concentration must be kept low. Hydrogen peroxide (see below) is poisonous because OH radicals may be formed from the hydrogen peroxide. The discoloration of papers by zinc-containing pigments is explained by the formation of OH radicals.[12] Zollinger[7] discussed results from the above-mentioned kinetic examinations in a broader framework. He pointed out that the diffusion rate of the compounds into the fibre is also important, besides the chemical reaction rate.

HYDROGEN PEROXIDE: IONIC AND RADICAL MECHANISMS

Ney[6] has done profound research in alkaline bleaching of cellulose fibres with hydrogen peroxide.

$H_2O_2 \leftrightarrow H^+ + HO_2^-$	Eq. 1B
HO_2^- + cellulose → oxidation products	Eq. 7B

Reaction 7B is slower than reaction 7C.

HO or HO_2 + cellulose → oxidation products	Eq. 7C

To minimize the destruction of cellulose, conditions must favour the ionic mechanism over the radical mechanism. Because of the high reactivity of the radicals, this can only be reached by preventing the formation of radicals. Reactions 5B and 2B have to be prevented:

$H_2O_2 \rightarrow 2OH$	Eq. 5B
$OH + H_2O_2 \rightarrow H_2O + HO_2$	Eq. 2B

Pieces of art contain traces of heavy metals. These metals catalyse (i.e. accelerate) the decomposition of the hydrogen peroxide:[13]

$$Fe2^{+}, Cu^{+} + H_2O_2 \rightarrow Fe^{3+}, Cu^{2+} + OH + OH^{-} \qquad \text{Eq. 8}$$

This is known by chemists as Fenton's reagent; for restorers it is known as corrosive green colour and corrosive iron gallotannate ink.[14] By reaction of the Fe^{3+} and Cu^{2+} ions with HO_2 radicals, the Fe^{2+} and Cu^{+} ions are recycled.

$$Fe^{3+}, Cu^{2+} + HO_2 \rightarrow Fe^{2+}, Cu^{+} + O_2 + H^{+} \qquad \text{Eq. 9}$$

By these reactions free oxygen is formed (bubbles). By the formation of bubbles, the structure of the cellulose fibre is destroyed mechanically.

By metal ions the radical reaction is further accelerated, resulting in a change from the ionic 7B to the radical 7C mechanism of oxidation. Because of this change in mechanism, gaseous oxygen is formed. This results in mechanical destruction. The quantity of OH radicals formed per time unit also increases, and this destroys the cellulose by oxidation (reaction 7C).

In contrast, there is no change in mechanism in the alkaline hypochlorite bleaching process if metal traces are present.

In this case, a radical mechanism always dominates. This mechanism is characterized by a low rate of formation of OH radicals, which means that the cellulose is only smoothly oxidized, even though aggressive radicals are present. The formation rate of OH radicals is low because of the slow formation from HOCl and OCl^{-}.

The mechanisms and the selectivity of the reaction of OH radicals with chromophores and lignin as compared with carbohydrates (cellulose) are still being investigated.[15-17] The selectivity is obviously influenced by the concentration of OH radicals.

For these reasons, I recommend the general use of the hypochlorite bleaching process. This conflicts with the pollution control campaign against chlorine.[18] The danger of chemical and mechanical destruction of the object to be restored is much too great by the hydrogen peroxide bleaching process. Traces of metal result in a change of the reaction mechanism because of catalysis of the decomposition of the hydrogen peroxide, which results in formation of a huge quantity of reactive radicals and a huge quantity of gaseous oxygen bubbles.

SUMMARIES

Classical Methods of Bleaching in the Restoration Workshop: The Role of the OH Radical

As such poisonous and burning gases as ozone and chlorine dioxide should be excluded in restoration workshops, the author discusses the reactions and the chemical kinetics of other processes as they are used by restorers for bleaching paper objects, mainly hypochlorite. Hypochlorites can safely be used for bleaching paper objects as long as a pH of > 9.5 is maintained.

Méthodes Traditionnelles de Blanchiment dans l'Atelier de Restauration: Le Rôle du Radical OH

Etant donné que les gaz toxiques et inflammables tels que l'ozone et le bioxyde de chlore devraient être exclus des ateliers de restauration, l'auteur discute des réactions chimiques et des cinétiques d'autres procédés tels qu'ils sont utilisés par les restaurateurs pour blanchir des oeuvres d'art sur papier: principalement l'hypochlorite. Les hypochlorites peuvent être utilisés sans risque pour blanchir des oeuvres aussi longtemps que le pH est supérieur à 9,5.

Die klassische Bleiche in der Restaurierwerkstatt. Die Rolle der OH-Radikale

Ausgehend von der Feststellung, dass giftige und brennbare Gase aus der Werkstatt des Restaurators verbannt werden sollten, wird die Reaktion und die Reaktionskinetik anderer Bleichprozesse diskutiert, hauptsächlich der Hypochlorite. Hypochlorite können ohne Risiko zum Bleichen von restaurierbedürftigen Objekten verwendet werden, vorausgesetzt das pH der Bleichlösung sinkt nicht unter 9,5.

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