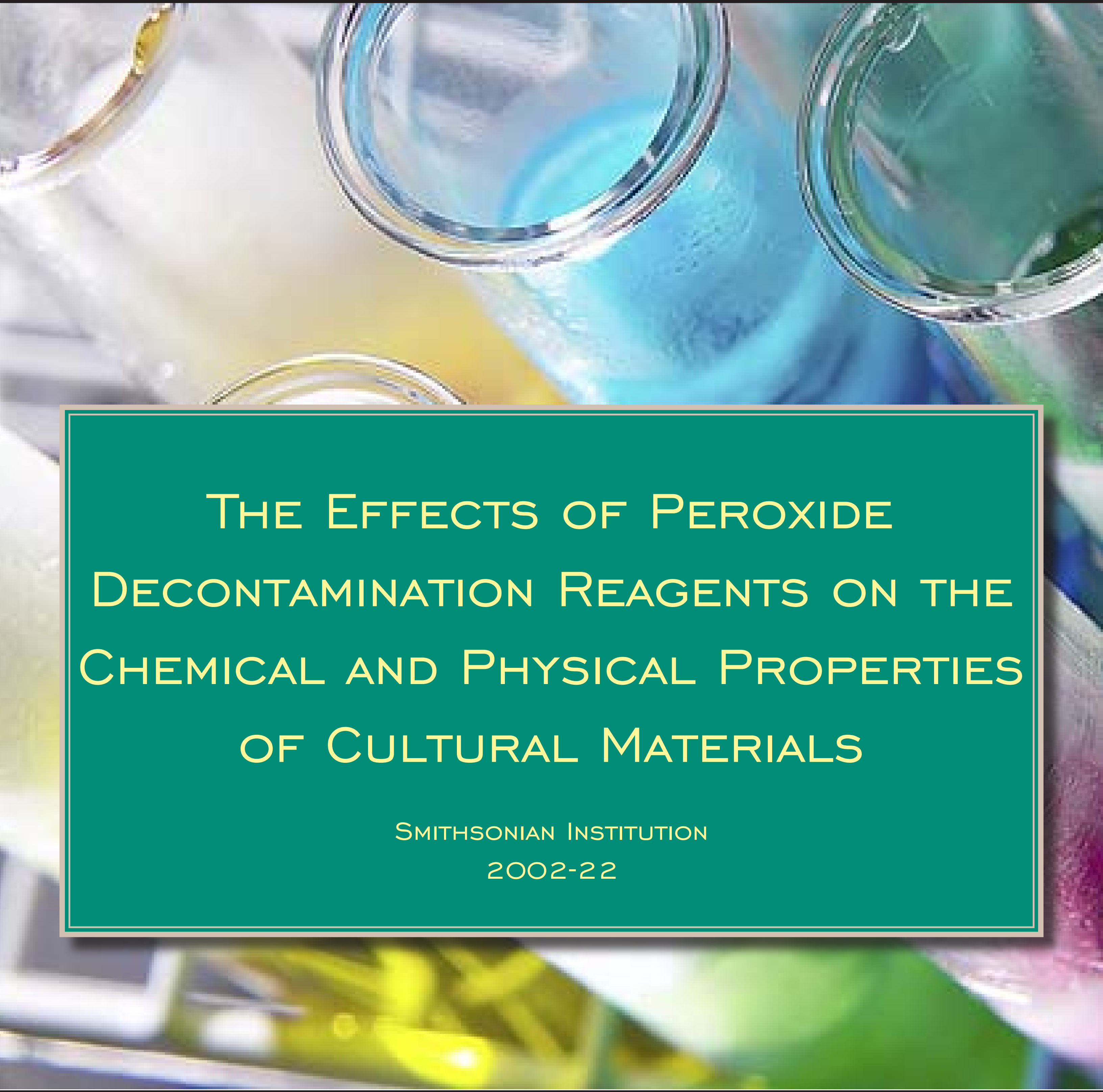
Materials Research Series



The Effects of Peroxide Decontamination Reagents on the Chemical and Physical Properties of Cultural Materials

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The Effects of Peroxide Decontamination Reagents on the Chemical and Physical Properties of Cultural Materials

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The Fall of 2001 saw terrorism on a scale not previously seen in the United States. Among the problems encountered were a series of anthrax contaminated letters sent to a number of locations including the offices of two Senators. This resulted in the contamination of the Hart Senate Office Building and its mail handling center as well as several mail sorting locations. Because of the scale of contamination, gaseous fumigation with chlorine dioxide was proposed as the method of decontamination for the Senate building. However, because of the aggressive oxidizing nature of this gas, there was concern about the possible effects on artwork and sensitive technical equipment as well as personal items such as photographs in the building. Tests of exposure to a number of quickly prepared test samples showed that damage such as fading of inks, dyes, and photographs did indeed occur [1]. Mitigation of the problem by such techniques as surface treatment with oxidizing agents also was considered. In the end, the building was fumigated with chlorine dioxide after possibly sensitive or valuable objects and items were removed. These were treated separately by a number of methods appropriate to the types of objects, including chemical treatment and mechanical decontamination (HEPA vacuum cleaning).

Chemical treatments to mitigate biohazards include the traditional agents such as hypochlorite bleaches, peroxide based agents such as that developed at Sandia National Laboratories for chemical and biological warfare agents, and Oxone®, a DuPont product whose active ingredient is potassium peroxymonosulfate. The efficacy of each reagent depends on its concentration, method of application, and duration of exposure [2]. For non-urgent situations, the time required for decontamination is not critical. In critical situations, however, effective action may be required in a relatively short time. For example, military guidelines generally require effective decontamination within one-half hour of application. The concentrations of the active agents in decontamination formulations generally are chosen so that they are effective in such a time frame. In the tests we conducted, we used standard concentrations and exposures of one-half hour in order to duplicate the types of exposure that might occur in practice.

While these compounds and formulations can be effective in the decontamination of a range of both chemical and biological agents, all of them are potentially damaging to many of the materials of objects encountered in offices and museums. Their use may be unavoidable, however. Because there is little data with which to evaluate the potential damaging effects of these treatments, we initiated a study to examine their effects on various materials so that informed decisions can be made about the use of these reagents in specific situations. The same reagent may not be appropriate in all cases. For example, one reagent may be the least aggressive in corroding metals but more aggressive in altering dyes, inks, or other organic materials. If decontamination of valuable or irreplaceable objects is necessary, damage may be unavoidable but may be minimized if the appropriate information is available.

A large variety of materials has been studied [3]. Separate samples were exposed to the decontamination reagents: a 3% hydrogen peroxide solution, a 0.58% sodium hypochlorite solution and a 1% potassium peroxymonosulfate (Oxone®) solution. Oxone® was donated by the Dupont Corporation, Wilmington, DE, USA.

Metals

A visual observation allowed us to see some corrosion on certain metals, while some of them were not affected at all [3].

	Oxone®	H_2O_2	NaOCl
Gold	=	=	=
Tin	=	=	=
Titanium	=	=	=
Silver	+++	=	+++
Iron	+++	=	++
Copper	+++	++	=
Brass	+++	=	=

Legend:
= indicates no changes before and after treatment
+ indicates a little change
++ indicates an important change
+++ indicates a dramatic change. In the case of inks, paints and photographs it indicates a drastic change or vanishing of color.

Oxone®, hydrogen peroxide and sodium hypochlorite can be used to treat gold, tin and titanium, because they have no effect on these metals. Hydrogen peroxide can also be used on silver, iron and brass, but it affects copper severely. Sodium hypochlorite can not be used on silver and iron but is allowed on copper and brass in the time frame of 30 minutes. Finally oxone® can not be used on silver, iron, copper and brass.

Figure 1: iron samples treated by immersion for 30 minutes in water, H_2O_2, Oxone® and NaOCl.

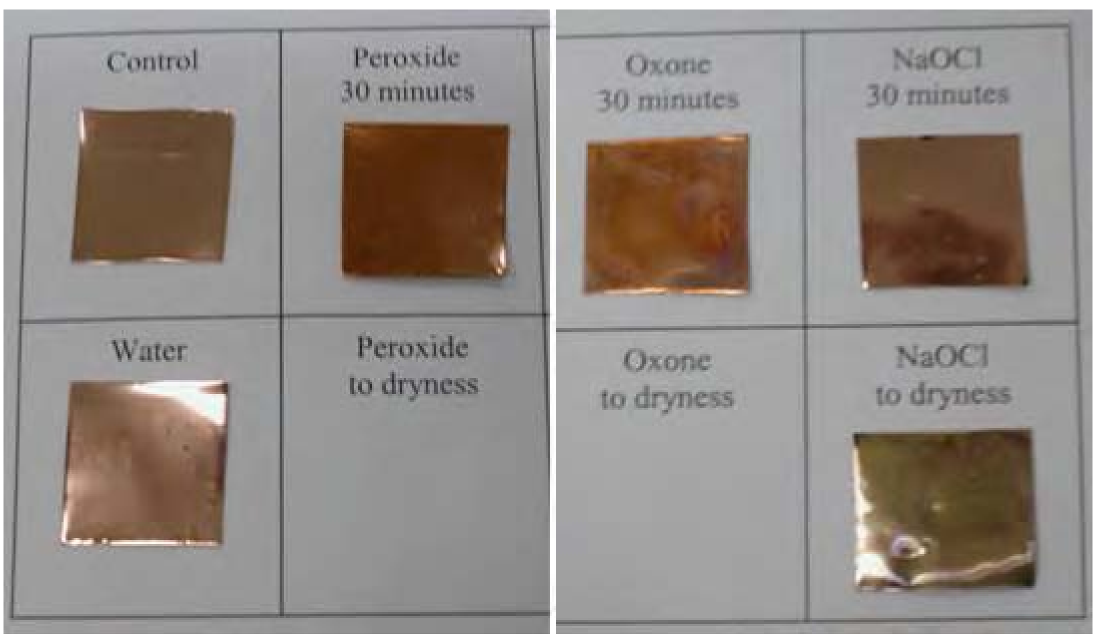

Figure 2: copper samples treated by immersion for 30 minutes in water, H_2O_2, Oxone® and NaOCl.

Inks

A large number of writing inks were treated [4]. A set of 60 inks were treated by the oxidizing reagents and more than 50 inks were analyzed after irradiation by an electron beam. Included among the inks examined were several samples of the BIC, Papermate, Pilot, and Skilcraft brands, and other pens found in the laboratory. The sample set represented a range of samples of ballpoint, fibre-tip, felt-tip and marker pens and pencils.

Name	Color	Oxone®	H_2O_2	NaOCl	Electron beam
Avery dennison Hi-liter	blue	+ + +	+ + +	+ + +	=
Berol non-photo verithin	blue	+	=	=	=
Bic commercial	blue	+ +	+	+ + +	
Bic courtyard Marriott	black	=	+	=	
Bic Mexico B6	Pink	=	=	+ +	
Bic Mexico B16	Purple	=	+	+ + +	
Bic Mexico B25	Green	=	=	+ + +	
Bic Mexico B31	Turquoise blue	+ +	+	+ + +	
Bic round stic fine USA	blue	+ + +	+ +	+ + +	+
Bic round stic medium	green	=	=	+ +	
Bic round stic medium	red	+	+	+ + +	=
Bic wide body mexico	black	=	=	+	+
China = MAAFS	black	+ +	+	+ + +	=
Col-erase 1272	brown	=	=	+	=
Crayola	green	=	=	=	=
Eberhard faber Japan	black	+ +	+ +	+ + +	=
Fisherbrand fine	black	+	+	+	=
Magnolia	blue	=	=	+ + +	=
Papermate	black	=	=	=	=

eraser mate med					
Papermate eraser mate med	red	+	=	=	=
Papermate med PT	blue	+	=	+ + +	+
Papermate med PT	red	+ + +	+ + +	+ + +	=
Papermate metal roller fine	black	+	+ +	+ + +	=
Papermate metal roller micro	blue	+ + +	+ + +	+ + +	=
Papermate metal roller micro	red	+ +	+ + +	+ + +	=
Papermate write bros med PT	blue	+ +	+	+ + +	=
Pilot explorer extra fine	black	=	+	+ + +	
Pilot explorer fine	blue	+	+ +	+ + +	
Pilot precise fine	blue	+ +	+ +	+ + +	
Pilot precise V7 rolling ball	blue	+ +	+ +	+ + +	=
Schwan stabilo	red	+	+ + +	+ + +	+
Sanford sharpie	black	=	=	+	
Sanford sharpie	red	=	+	=	
Sharpie fine point	blue	=	=	+	=
Sharpie fine point	red	+	+	+	=
Sharpie ultra fine point	black	+	=	+	=
Skilcraft cushion grip fine	blue	+	=	+ +	
Skilcraft felt	blue	+ + +	+ + +	+ + +	+
Skilcraft felt	black	+ + +	+ + +	+ + +	=
Skilcraft felt	green	+ + +	+ + +	+ + +	=
Skilcraft	blue	+	=	+ + +	+

USA					
Skilcraft-US government fine	blue	+	=	+ + +	+
Skilcraft-US government fine	black	=	=	+	+
Skilcraft-US government med	blue	+	=	+ + +	+
Skilcraft-US government med	black	+	=	+ +	=
Skilcraft-US government med	green	+	=	=	=
Skilcraft-US government med	red	+	=	+ +	=
Skilcraft highlighter	blue	+ + +	+ + +	+ + +	=
Skilcraft highlighter	green	+ +	+ + +	+ + +	=
Skilcraft highlighter	pink	=	=	+ +	
Skilcraft highlighter	yellow	=	=	+ + +	=
Skilcraft marker	black	=	=	+ +	=
Skilcraft marker	red	+	+	+ + +	+
Staedler lumocolor	blue	+	=	+ + +	
Staedler lumocolor	black	=	=	+ + +	
Staedler lumocolor	green	=	+	+ +	

Immersion in hydrogen peroxide left the inks unchanged or slightly diminished in intensity. About one third of the inks treated with Oxone® showed obvious differences: the color faded, disappeared or changed. Sodium hypochlorite is the most aggressive reagent: all the inks were affected, except Crayola green and Berol blue. The color disappeared in one third of the cases and faded in the other cases.

A certain number of inks totally disappeared because of their solubility during the immersion, this was the case with Papermate metal roller micro blue, Skilcraft highlighter blue, Avery Dennison Hi-Liter blue, Skilcraft highlighter green, Skilcraft felt blue, Skilcraft felt green, Skilcraft felt black, Schwan stabilo red and Papermate metal roller micro red.

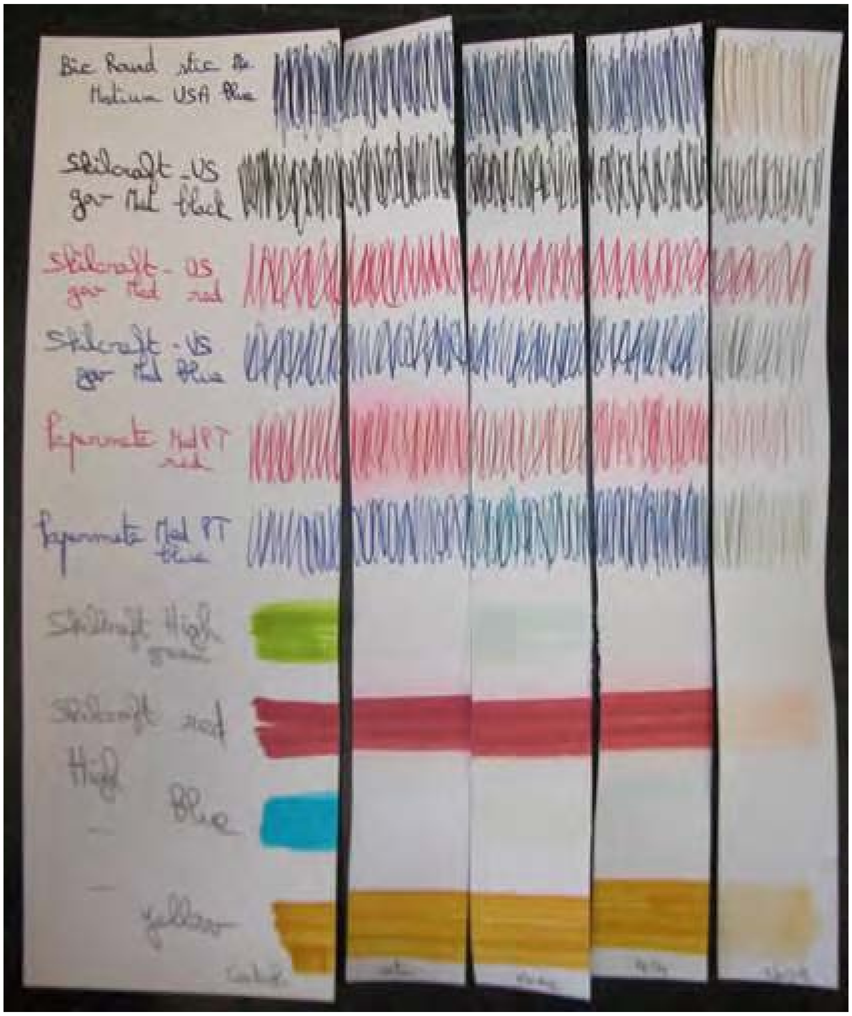

Figure 3: samples of writing inks treated by immersion for 30 minutes in water, H_2O_2, Oxone® and NaOCl.

Cellulose

Paper

The paper samples chosen for the treatment were some new white paper, a recent newspaper from 2002 and two naturally aged books, a bible from 1838 and a cookbook from 1851 [3].

	Oxone®	H_2O_2	NaOCl
Whatman	=	=	=
Newspaper	+++	+	+
Bible	+	=	+
Cook book	+	=	+

The newspaper yellowed when treated by Oxone® and sodium hypochlorite while the 1838 Bible and the 1851 cookbook papers were bleached. Hydrogen peroxide had few apparent effects on the specimens of paper.

Oxone® must be avoided, especially on paper like newspaper, because it is made of wood pulp, rich in xylan, which is easily degraded to yield xylose. Hydrogen peroxide is the least aggressive reagent.

Cotton

The treatments by Oxone®, hydrogen peroxide and sodium hypochlorite did not affect the appearance of the samples of modern cotton textiles [3].

	Oxone	H_2O_2	NaOCl
greige cotton duck	=	=	=
bleached cotton print cloth	=	=	=

The analyses by gas chromatography did not show any differences. Apparently little material was leached or altered during the treatment.

Collagen

The effects on collagenous materials were tested on four specimens obtained from our reference collection: calfskin vellum, goat vellum and sheepskin parchment of modern manufacture, and hide glue, which is from cow skins and was cast as a thin film 8 years previously [5].

	Oxone®	H_2O_2	NaOCl
Calfskin vellum	+	+	+
Sheepskin parchment	+	+ +	+ +
Goat vellum	=	=	+
Hide glue	=	=	+ + +

Most of the time, we noticed a change of color on the samples of goat vellum, calfskin vellum, sheepskin parchment and hide glue. Generally the treatments yellowed the samples. They bleached them in only two cases (sheepskin parchment treated by Oxone® and hydrogen peroxide). Methionine is the most affected amino acid.

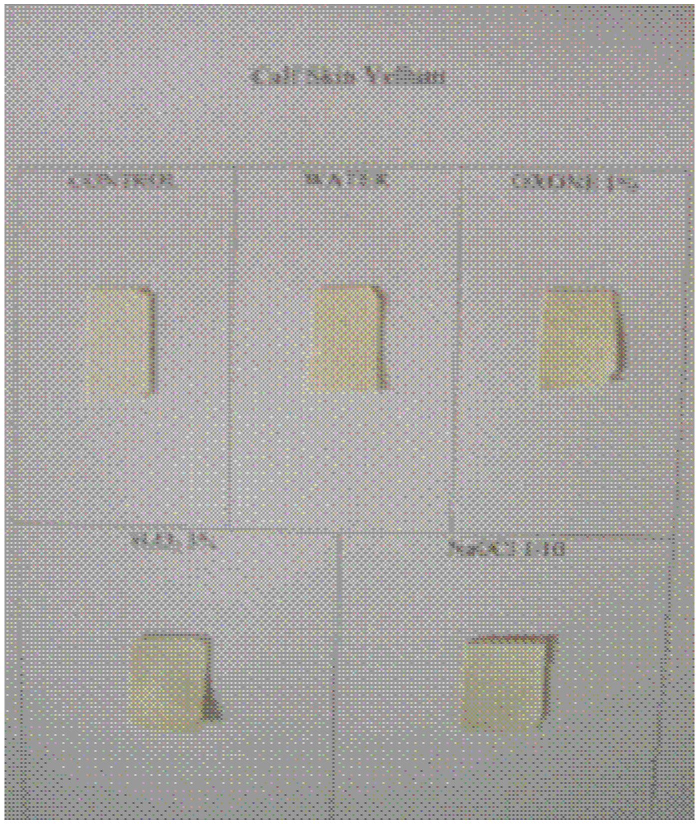

Figure 4: calf skin vellum samples treated by immersion for 30 minutes in water, H_2O_2, Oxone® and NaOCl.

Keratin

Keratinous materials consisted of two specimens of wool fabric, and one of dog hair. The textiles are of modern manufacture. The dog hair was taken from a female Siberian husky.

	Oxone		H_2O_2		NaOCl	
	Visual aspect	Amino acid sequence	Visual aspect	Amino acid sequence	Visual aspect	Amino acid sequence
ISO wool adjacent fabric	+	+	+	=	++	++
100% wool flannel	++	+	=	=	+++	++
Dog hair	+	++	++	=	+++	+

The samples of wool treated by Oxone® and NaOCl yellowed, slightly with Oxone® and drastically with NaOCl. The samples of wool treated by H_2O_2 bleached. The dog hair is drastically affected by NaOCl only: the reagent stuck yellowed the hair and caused it to stick together. Oxone® and NaOCl induce changes in the amino acids profile: formation of cysteic acid, reduction of tyrosine and methionine.

Hydrogen peroxide is the best reagent, oxone and NaOCl must be avoided.

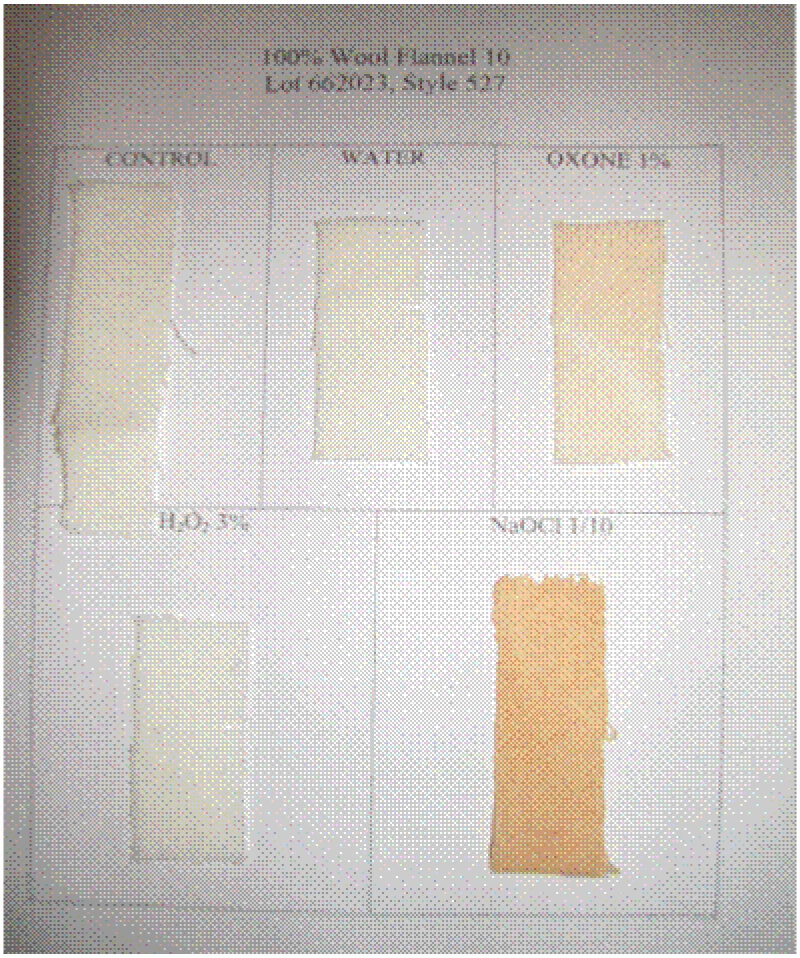

Figure 5: wool samples treated by immersion for 30 minutes in water, H_2O_2, Oxone® and NaOCl.

Silk fibroin

Materials consisted of two specimens of silk fibroin modern manufacture.

	Oxone®	H_2O_2	NaOCl
ISO silk adjacent single fiber	+	=	+++
Silk habutae	+	=	+++

The samples of silk treated by Oxone® and NaOCl yellowed, slightly with Oxone® and drastically with NaOCl. Hydrogen peroxide is the best reagent.

Figure 6: silk samples treated by immersion for 30 minutes in water, H_2O_2, Oxone® and NaOCl.

Marble

Three different marbles were tested: a kitchen marble, a marble from a building in Philadelphia and marble chips from Fisher. Marble was ground into powder and cut into chips. The powder and chips were weighed before and after immersion to evaluate the loss of weight by dissolution.

	Oxone®	H_2O_2	NaOCl
Kitchen marble	++	+++	+
Building marble	+++	++	=
Fisher marble	+++	=	=

Oxone® and hydrogen peroxide are acidic reagents. Because of this, they attack marble more easily, causing dissolution accompanied by release of CO_2. Oxone® is the more acidic, and must be avoided in the treatments.

Oil paints

Three kind of oil paints were tested: malachite (2 $CuCO_3$, $Cu(OH)_2$), a green basic copper carbonate; alizarin (1,2-dihydroxyanthraquinoxe), a red natural pigment from madder plants; and lead white (2 $Pb(CO_3)_2.Pb(OH)_2$), a white basic lead carbonate.

	Oxone®	H_2O_2	NaOCl
Malachite	=	=	++
Alizarin	+	=	+
Lead White	=	=	+++ (brown)

Sodium hypochlorite must not be used to treat the oil paint samples, because it affects the color and the fatty acids profile. NaOCl, which is a basic reagent, attacks the diacids. Hydrogen peroxide is the best reagent to use.

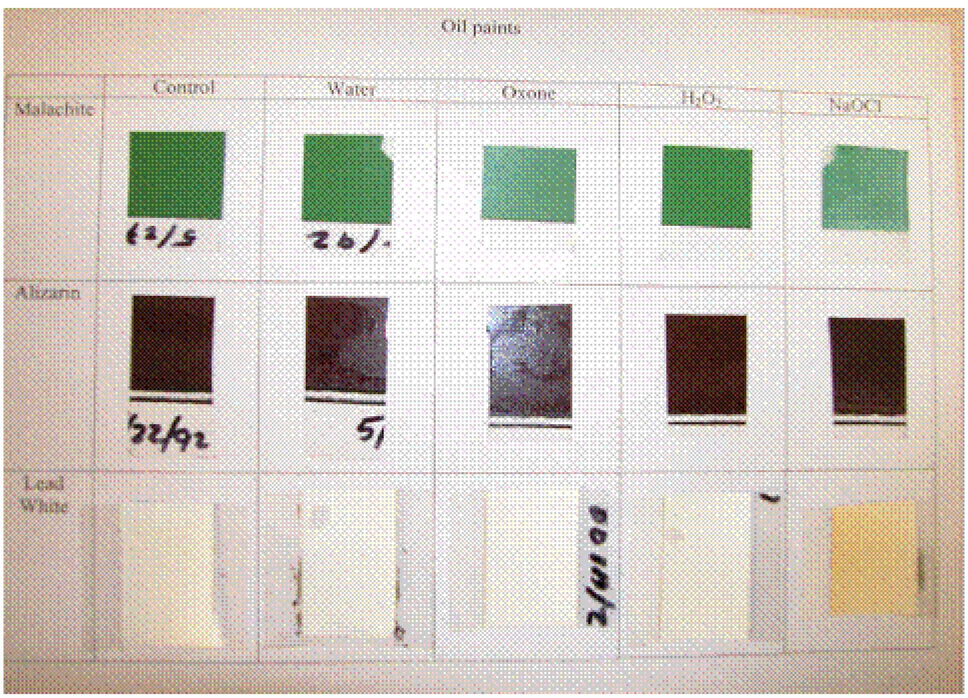

Figure 7: oil paints samples (malachite, alizarin and lead white) treated by immersion for 30 minutes in water, H_2O_2, Oxone® and NaOCl.

Photographs

Pictures developed on Kodak paper were tested by color.

	Oxone®	H_2O_2	NaOCl
White	+ +	+ +	+ + +
Blue	+	+	+ + +
Black	+ +	=	+ + +
Green	+ + +	=	+ + +

Hydrogen peroxide is the best reagent to use.

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