

Pollution in the photographic archive - a practical approach to the problem

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Abstract

It has been known for about 150 years that pollutants can cause fading or other types of damage to photographic materials. A recent case story from Norway is just another example of air pollution destroying photographic images, in this case the source was fresh wall paint. Pollution can be the cause of many different types of deterioration, depending of different chemical reactions. A number of the most common pollutants, their sources, and effects are outlined. While concentration normally is the unit used for quantifying air pollution, total doses should be the correct unit, because pollution-related deterioration is an accumulative process.

A systematic strategy for protecting photographic materials from pollution is reviewed, consisting of the five stages of control: "Avoid sources of the agent, block the agent, detect the agent or its effects, respond to the agent, and recover from the effects of the agent on the object". It is concluded that it is beneficial to concentrate on avoiding sources of pollutants in the first place, rather than to have to carry out the following actions, which are more time consuming and expensive, if possible at all.

Introduction

Almost ever since the invention of photography the influence of the air quality on the stability of photographic materials has been a subject of study. Already in the 1850's the British Fading Committee of the Royal Photographic Society were investigating the reasons as to why photographic prints would fade. Among other things, the committee found that prints exposed to humid air polluted with hydrogen sulphide would fade, especially if the print wasn't rinsed throughout or toned proper, and that gold toning could improve permanence. In our century it was especially the occurrence of red spots on microfilms around 1960, the so-called micro blemishes, woke the awareness of pollution and its effect [1]. Pollution migrating from poor quality paper or plastic folders was often found to be the cause of this. Also, other pollution sources have been suggested: automobile exhaust fumes, pollution from nearby factories, off-gassing from furniture, or from fresh paint [2,3]. Finally the photographic materials themselves can be the source of pollution. The best-known examples are the emission of acetic acid from cellulose acetate film base, and nitrogen oxides from cellulose nitrate film bases. A less violent but still considerable emission of nitrogen oxides will occur from collodion plate emulsions.

A case history

There are numerous case histories about just how aggressive pollutants actually can be to photographs. This is the most recent case the author has knowledge of:

At the Norwegian Museum of Photography - Preus Fotomuseum, an exhibition of the Norwegian photographer Marie Høeg was curated in 1997. The prints were contemporary fibre base prints after the original 19th century negatives. The exhibition was travelling to other museums and galleries in Norway, and at one museum a frame glass was broken, and therefore completely removed. For unknown reasons, instead of replacing the glass, the picture was simply exhibited without glass which is why this print was openly exposed to the surrounding air, while the other prints were protected by their framing. The time of that exhibition was during a hot summer, and after a few weeks all high-density areas in the openly exposed print were faded to a brown/yellow colour. It turned out that the gallery walls were newly painted with oil paint, why a high concentration of oxidizing gases probably has been present in the air. Luckily in this instance the print was just a copy that could be replaced [4].

The many aspects of pollution

In general, it must be emphasized that the issue 'degradation of photographic materials due to pollutants' is not simple, but consists of numerous issues. Firstly, there are many different types of materials present in the various photographic techniques, and secondly there are many different pollutants found in the environment. Therefore, the chemical deterioration processes are very varied: there are for example the micro blemishes mentioned in the introduction which are caused by redox-reactions between the image silver in the photograph and peroxides from the surrounding environment, forming thin layers of colloidal silver on the photographic emulsion. A totally different problem is the degradation of cellulose acetate film which is an autocatalytic release of acetic acid from the cellulose esters in the film base, causing the base to become brittle and shrink, the so-called "vinegar syndrome". However, in the end both of these very different forms of decay will have the same result: Loss of image information.

Table 1 lists a number of these different pollutants, their sources, and their effect on photographic materials. This list is by no means complete, and one important aspect of pollution is not dealt with here: the effects of pollutants multiply in combination. This often causes more aggressive deterioration than single pollutant attacks.

Pollutants	Source	Effect on photographs
Sulphur compounds	Low quality paper enclosures Adhesives Carpets (with rubber) Bioeffluents Outdoor (combustion and natural sources)	Fading of silver images Brown/yellow discolouring of silver images Fading of colour images Brittleness of paper and emulsion
NO _x	Cellulose nitrate film Collodion photographs Outdoor sources (traffic)	Fading of silver images Fading of colour images Brittleness of paper and emulsion Brittleness of nitrate film base
Other oxidizing gases (O ₃ , H ₂ O ₂ , etc.)	Low quality paper enclosures Fresh paint Office machines Outdoor (traffic and natural sources)	Fading of silver images Fading of colour images Brittleness of paper and emulsion
Carbonyl pollutants (acids, aldehydes)	Cellulose acetate film Wood and woodboards Various building materials	Brittleness and shrinkage of acetate film base Brittleness of paper and emulsion

Table 1: A selection of the most common pollutants in museum and archive environments, their sources, and possible effect on photographic materials.

Pollution thresholds

Only a few research projects have been made to determine safe levels of pollutants in air in relation to photographic materials. The levels suggested until now seem to relate more to how low detection levels today's technology allows, rather than to the actual sensitivity of the photographic materials. An example of this is a quote like "use best control technology".

A typical misunderstanding or inaccuracy is to refer to safe levels expressed in concentration of pollutants in air, either volume/volume (parts per billion or $\mu\text{L}/\text{m}^3$) or weight/volume ($\mu\text{g}/\text{m}^3$). This only expresses instant value, and without including a time and airflow factor this has no meaning, because - as for exposure to light, damage caused by pollution is accumulative. Safe levels should therefore more correctly be expressed in a total dose allowed to reach the photograph, as $\mu\text{g}/\text{cm}^2$ surface. Much research has yet to be accomplished before these possible safety levels are found, and before easy and practical methods to measure this from air can be developed.

Standardized terms describing materials suitable to be in contact with photographs: enclosures, boxes, or mounting materials are on the contrary quite well developed. The standards of the American National Standard Institute advise on a number of chemical qualities that enclosure materials must meet to be of archival quality, such as pH-value, content of sulphur, chlorine, lignin, alkaline reserve etc. [5]

A practical approach to deal with pollution

The talk about concentrations in air, doses etc. is for most museum staff still a rather hypothetical subject, compared to everyday work life. What really is important is to know how

to handle situations arising from pollutants present in the archive environment, and to have a work strategy ready at hand. One such very useful strategy is the "Framework for Preservation of Museum Collections" developed by researchers at the Canadian Conservation Institute [6]. For all kinds of agents of deterioration the situation is handled through five stages of control:

1. **Avoid** sources of the agent
2. **Block** the agent
3. **Detect** the agent or its effects
4. **Respond** to the agent
5. **Recover** from the effects of the agent on the object

Below each stage of control is briefly reviewed with comments in regard to pollution as the agent of deterioration:

1: Avoid sources of the agent

"Avoid" is really the keyword here. If pollution is avoided in the first place there will be no pollution-related deterioration, and no need to take the following more complicated and expensive "block", "detect", "respond", and "recover" actions. New construction materials to be used in an archive should be tested for their possible emission of pollutants. Also, new enclosure materials should be tested for their suitability. On arrival new photographic documents for an archive should be examined, and emissive materials like collodion plates, cellulose nitrate- or acetate-based negatives should be identified and kept separate from then on.

2: Block the agent

If it is not possible to completely remove all sources of pollution, arrangements must instead be taken to prevent the pollutants from reaching the photographs, or to mitigate the deteriorating effect by other means.

For all new photographic materials produced for an archive, actions such as toning of silver images will be a very effective method. By toning the metallic silver image is transferred into a more stable compound, with, e.g. gold, selenium, or sulphide. Research suggests that certain polysulphide toners as IPI Silver Lock ensures the highest resistance for oxidative attacks on silver images [7].

In one particular case avoiding the pollution source is impossible: when the photographs themselves are the sources. The photographic materials should of course be kept separately from other photographs, but they will still be a threat to themselves. "The vinegar syndrome" is such an example. Actions to mitigate emission are done by controlling the environment, by keeping the climate conditions cold and dry. This way the speed of the chemical deterioration and by this also the rate of emission of acetic acid is slowed down. Also air cleaning materials as zeolite-containing paper or boards can be used to interleave the film sheets for catching the emitted acids.

Ventilation is probably the best method to prevent that high build-ups of corrosive gasses occur, why it is important not to use very airtight boxes or enclosures for materials, which let off such gases. A high ventilation rate will effectively remove emitted pollutants before they can cause damage to other materials. This could be combined with recirculating the air through filters.

3: Detect the agent or its effects

As soon as a problem is evident, it is vital to detect and remove the pollution source, or if not possible, to remove the photographs from the source. Pollutants in high concentrations will often simply be smelled, as fresh paint or high emissions from cellulose nitrate or acetate film are. Much more difficult is the detection of low but constant concentrations. Photographic images unfortunately are good monitors themselves, this means that pollution problems often are detected quite fast by the deterioration of the images. It has been desired for long to develop simple monitors that instantly gave warning of the presence of air pollutants. One such monitor is the AGFA Gevaeret colloidal silver film described by Weyde [2]. This monitor for oxidizing gases is a polyester film with an emulsion containing colloidal silver grains, which will fade or darken if exposed to oxidizing agents. An AGFA logo was coated over the emulsion on the original monitors, and if fading/darkening occurred, because a monitor was exposed to pollution, the logo became visible. This monitor is not made anymore, but raw film sheets can still be purchased [8].

The author is at the moment experimenting with pollution detectors made of step tablets copied on photographic Print Out Paper. This type of emulsion is much like the AGFA Gevaeret colloidal silver film, with an image layer of very small silver grains. These grains should be more sensitive to pollutants than the larger silver grains found in contemporary photographs, therefore fading or darkening of the step tablet should be an early warning sign compared to such materials. The change can be determined by densitometric

measurements. The disadvantage with both these methods is that the estimation for threshold doses is very vague; Weyde noted that if darkening occurs after 'weeks or a few months' there will be danger for the stored photographs, but if darkening occurs only after 'one or more years', there does not seem to be serious danger for the stored photographs [9].

A more accurate, but also more complicated monitoring method, is to sample pollutants from the air on an absorbent material, and then analyse the composition. This can be done either in active mode (sucking a known volume of air through a sampling tube with an absorbent material) or by passive mode (to let air diffuse over the monitor during a certain time). Analyses are then performed by various chromatographic methods. The drawbacks of these methods are that they do not give a direct reading, they are expensive, and not easy to perform. However, especially the passive sampling method is becoming more common also in the museum and archive world.

The future solutions are real-time pollutant monitors, possibly integrated with other environmental sensors as temperature and humidity probes. Today such systems are available but very expensive. Also, the detection limits might not be low enough just yet. One possibility are photo-acoustic IR-monitors, which identifies gases from their absorbing of specific parts of the infrared spectrum [10]. Piezoelectric sensors (mass-dependent resonance frequency measurement of metal-plated crystals) are another system, measuring the thickness of corrosion layers on silver and copper plated sensors exposed to the air [11]. The photo-acoustic IR-monitors are measuring concentration, while the piezoelectric sensors are measuring accumulative doses.

The suitability of materials to be in contact with photographic materials can be tested with the 'photographic activity test' [12]. This test detects possible interaction (fading or staining) between an enclosure and photographs, by exposing samples of the enclosure material to detectors of photographic paper, and AGFA Gevaeret colloidal silver film, in a controlled and accelerated climate (70°C, 86% RH, 15 days).

"Detect" does also mean to look for deterioration of the materials in one's collection, which can be caused by air pollution. Collections should be condition-surveyed on a regular basis. As photographic collections often have very big volumes, survey models with sampling smaller but representative numbers (between a few hundred and one thousand) are proposed [13]. Surveying a collection is a very important part of managing a collection, unfortunately often neglected. As photographs are very good air pollution-monitors themselves, simply by looking at the materials often is how problems are first identified, purely by coincidence.

4: Respond to the agent

After pollution damage has been found, and the first round of ("block" and "detect") actions have been carried out, it is important to evaluate these actions. Do they work? Should they be improved?

Evaluate your "avoid" actions: Are all polluting materials removed from the archive? If not, respond by doing so.

And continue in the future to test all new materials that are to go into the archive room. Separate nitrate, acetate, and collodion materials from other photographic materials.

Evaluate your “block” actions: Evaluate the quality of the protective toning of new photographic materials by test methods like ‘the peroxide test’ [14]. Evaluate the protective effect of the use of zeolite containing enclosures, of ventilation, of air filtering, etc. by surveying the collection at regular intervals. Is there any effect or should you respond by improving your actions and maybe also by improving the climate?

Evaluate your “detect” actions: Does the smell disappear? If you are monitoring air pollutants, is the level decreasing? Is your method sensitive enough, and are you monitoring for the right pollutants? If the used enclosure materials fail the ‘photographic activity test’, respond by repackaging the photographs into new and better enclosures. If you again detect pollution problems during a collection survey, respond with new and improved “avoid” and “block” actions.

5: Recover from the effects of the agent on the object

In general, damage caused by air pollutants is hard to restore. Faded silver images might be conserved chemically; however, this is a time-consuming task. There are no known conservation techniques for faded colour images today.

Not only the photographic materials will respond to air pollutants. Also, the enclosures around the photographs will absorb pollutants and become acidic. So a beneficial recovery action after several years in a highly polluted environment is to re-pack the photographs into new high quality archival enclosures. The new enclosures should fulfil the recommendations in the ANSI standard IT9.2-1991 [5].

Materials especially vulnerable to air pollution as nitrate and acetate films can be copied to ensure the image information is not lost. This action will conserve the image information; however, it must be emphasized that this is not conserving the photograph as an object. The new image will never be more than a copy. As it gets harder and harder to get the right photographic materials for duplicating negatives, digital imaging is a commonly used solution for coping nowadays.

Conclusion

It is important to realize that pollution is caused by a broad range of substances causing a broad range of chemical reactions. Also the combination of different pollutants can accelerate deterioration more rapidly than single attacks. Therefore detection methods that measure the accumulative interaction between the total of pollutants in the environment and the monitors are more valid than monitors only measuring the concentration of single pollutants. Such monitors can be colloidal silver grain emulsions which fade when exposed to pollution, or real-time monitors measuring the build up of corrosion layers on its sensors.

One approach to tackle the threat of pollutants in the archive environment is the Canadian model “Framework for the Preservation of Museum Collections”. Dividing the approach into five stages of control - “Avoid”, “Block”, “Detect”, “Respond”, “Recover”- it is very important to establish so good “Avoid” actions that hopefully it never becomes necessary to have to carry out “Recover”- actions. “Avoid”- actions should include tests of enclosure materials by the ‘photographic activity test’, and separation of highly emissive photographic materials from the rest of the archive stock. Construction materials intended to be used in the archive should at the very least not emit or generate any of the pollutants listed in table 1. The archive environment should constantly be monitored, and surveys of the collection’s condition should be carried out on a regular basis. If the ongoing preventative measures show to be inappropriate, respond by improving them. Conservation of pollution-damaged photographs is a difficult task, if possible at all. Preventing pollution problems in the first place always will prove more beneficial.

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Biography

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