# Correlation between Gas-resistance Testing Method and Image Deterioration in Indoor Displays: An Analysis of Phenomena Occurring in Mixed-gas Test with Ozone

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## Abstract

*Gas resistance is an important element in image permanence. We studied the effects of $O_3$, $NO_2$ and $SO_2$ exposure on several imaging materials, such as inkjet, silver halide and other printing materials and observed the fading of those imaging materials under actual indoor display conditions. We found that a correlation exists between image deterioration in the actual display and the accelerated gas exposure test and identified problems in the mixed-gas tests, including, for example, a rapid reaction between $O_3$ and $NO_2$ under accelerated conditions. We will discuss the effects of this reaction on the estimation of print life.*

## Introduction

The main environmental factors that contribute to image deterioration include light, heat, humidity, and gases. Prints today boast sharply improved resistance to heat and humidity (dark storage permanence) and to light. However, when images are displayed as is without framing, gas resistance may become the major factor in image deterioration. This is especially true in the case of dye-based inkjet prints, for which the improvement of gas-resistance continues to be an important issue. How one evaluates gas resistance assumes great importance in the attainment of a guide towards this end.

In the case of the indoor display of inkjet images consisting of dye-based ink on porous media, papers have been published on deterioration that occurs in images directly exposed to indoor pollutant gases. These include papers that mainly correlate deterioration with $O_3$[1-3] and studies on the contribution of $NO_2$ to image deterioration,[2-4] as well as papers that propose experiments using a mixture of $O_3$,$NO_2$ and $SO_2$ as atmospheric pollutant gases.[5]

This paper presents the results of tests using single gases and mixtures of three gases and their correlation with the deterioration in actual display. It also provides an analysis of phenomena that occur in mixed-gas tests and an explanation of the associated problems.

## Experiment

We subjected unframed print samples to accelerated gas tests and displayed identical unframed print samples as is inside different houses. We then compared the samples. For the mixed-gas tests, we focused attention on whether a reaction occurred between the different gases and whether such a reaction produced negative effects.

### *Equipment*

For samples, we used two types of inkjet prints printed with representative, commercial dye-based inks, and prints made on silver-halide color paper. Measurement patches consisted of gray steps ranging from minimum density to maximum density, as well as pure-color patches for YMC.

Sample A: Inkjet print produced with dye-based inks manufactured by Company A

Sample B: Inkjet print produced with dye-based inks manufactured by Company B

Sample C: Print produced on silver-halide color paper manufactured by Fujifilm

The various inkjet prints were produced on different brands of inkjet printers using the manufacturers' own brand of inks and photo-quality paper.

### *Accelerated Gas Tests*

The single-gas tests were conducted using three gases, $O_3$, $NO_2$, $SO_2$, and the mixed-gas tests were conducted using mixtures of the same three gases. The tests were done with a specially ordered gas corrosion test instrument made by Suga Test Instruments Co., Ltd., which provided the ability to precisely control gas concentrations, temperature and humidity within the test chamber. The methodology used for the mixed-gas tests was adopted from a paper[5] published in Proceedings of IS&T's NIP20. A method of controlling the concentration of each gas within the chamber was used in the conduction of the tests, as follows:

- $O_3$ test: 1 ppm, 24°C, 60% RH
- $NO_2$ test: 20 ppm, 24°C, 60% RH
- $SO_2$ test: 1 ppm, 24°C, 60% RH
- Mixed-gas test: $O_3$,$NO_2$,$SO_2$=0.3,1.8,0.1 ppm, 24°C, 60% RH

### *Indoor Displays*

Prints identical to those subjected to the accelerated gas tests were displayed inside several houses in a such a way that exposed them to air, but not to light, which allowed us to observe their deterioration by gases in the actual indoor display. We used filter badges to measure the concentration of indoor pollutant gases within the room at the each display location and data loggers to measure temperature and humidity.

- $O_3$ meter: Model 3300 (Ogawa Syoukai KK.)
- $NO_2$ and $SO_2$ meters: Handy SONOx (Green Blue Corporation)

## Results and Discussion

### Comparison of Image Deterioration in Accelerated Gas Tests and the Deterioration in the Actual Indoor Display

We compared the deterioration that occurred in Samples A to C during the accelerated gas tests with the actual indoor deterioration in the displayed samples. The estimated average indoor gas concentrations that we used to calculate the correspond number of exposed years were: $O_3$: 4.6 ppb, $NO_2$:15 ppb, $SO_2$:1 ppb.[1,3,6] In the mixed gas tests, we calculated the estimated number of years for each sample on the basis of the $O_3$ concentration. The natural elapsed time was 1 year for Samples A and B, and 3 years for Sample C. The average annual concentration of $O_3$ was 10 ppb in Household X, 7 ppb in Household Y and 3 ppb in Household Z. A kerosene heater was used during the winter in Household Z (Figure 1-3).

#### *Deterioration in the Actual Display*

Compared with silver-halide paper, which showed little deterioration even after 3 years, there was progressive color fading in the inkjet prints after 1 year. The order (for amount of fading) of the test samples was A>B>C.

#### *Accelerated $O_3$ Gas Test*

In the accelerated $O_3$ gas test, with the $O_3$ concentration set at about 220 times that of the natural environment (=1000/4.6), the deterioration in the actual display and fading order of the samples (A>B>C) was basically reproduced. This result corresponds with the previous finding[1-3] that identifies $O_3$ as the determining factor in the actual indoor fading.

#### *Accelerated $NO_2$, $SO_2$ Gas Tests*

No significant color fading was confirmed in Samples A to C even after exposure to $NO_2$ or $SO_2$ for the equivalent of several years. At present, we do not consider $NO_2$, unlike $O_3$, to have a simple or direct effect on images, and we consider $SO_2$ not to be a major factor in deterioration.

#### *Mixed-Gas Tests*

Compared with the actual indoor fading, the accelerated mixed-gas tests produced differences in the order of fading of color and order of the samples, as follows.

Sample A: Deterioration in the mixed-gas tests approximated the deterioration in the actual display and YMC deterioration order of the displayed prints at locations where the average $O_3$ concentrations were close to the standard values calculated for the estimated number of years.

Sample B: Compared with the deterioration in the actual display and deterioration in the $O_3$ gas tests, the rate of deterioration in the mixed-gas tests for yellow and cyan were reversed (especially at gray-patch). In the mixed-gas tests, the deterioration order for YMC did not match that for actual indoor fading, but it did match that of the $O_3$ gas tests.

Sample C: In the mixed-gas tests, Sample C fading that was not observed in actual indoor deterioration was observed after the equivalent of 3 years of exposure. The deterioration order of these samples, including the results of the mixed-gas tests for Samples A and B after an elapsed time equal to 3 years, was A (worse)>C>B, which did not match that of the deterioration in the actual display.

As these results show, the behavior in which the actual indoor deterioration was not reproduced in the accelerated mixed-gas tests was seen for both inkjet prints and silver-halide paper prints. Below, we will discuss how these inconsistent results were obtained in relation with problems associated with the mixed-gas tests.

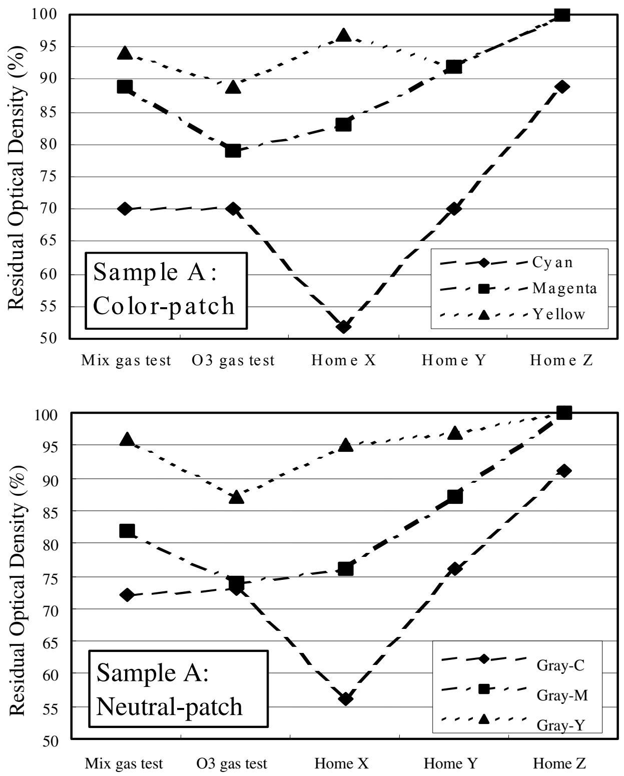

*Figure 1. Residual optical density of Sample A which was exposed to accelerated gas tests or displayed indoors for a year.*

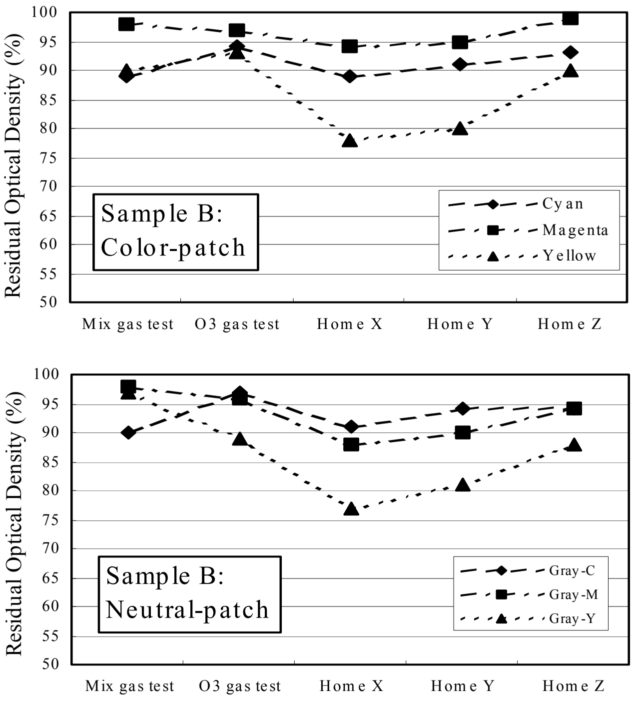

*Figure 2. Residual optical density of Sample B which was exposed to accelerated gas tests or displayed indoors for a year.*

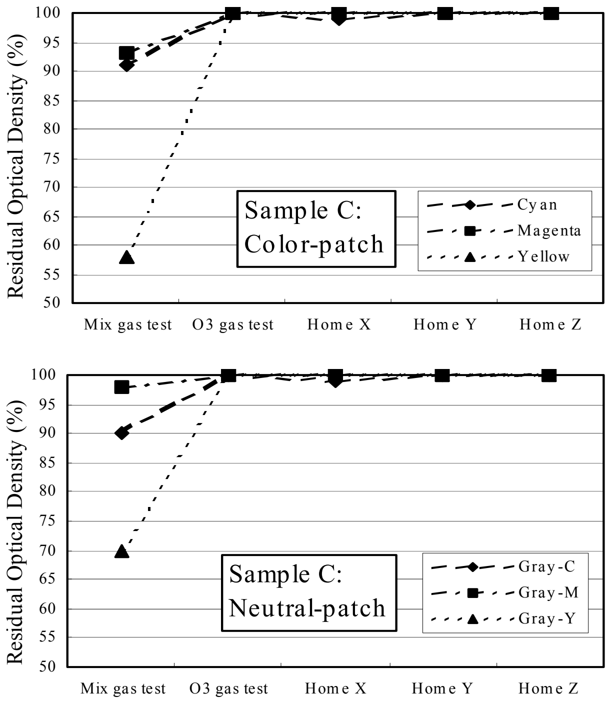

*Figure 3. Residual optical density of Sample C which was exposed to accelerated gas tests or displayed indoors for three years.*

## *Analysis of Phenomena Occurring in Mixed-Gas Tests*

### *Gas Concentration Inside the Chamber During Mixed-Gas Tests*

Although the actual mixed-gas tests were operated with concentrations of each gas were controlled within the chamber, for analysis of phenomena occurring in the mixed-gas tests, we controlled the amount of each gas prior to injection into the test chamber to measure the concentrations after the gases were injected constantly into the chamber. In this way, we were able to confirm the extent to which the original quantities of each gas were retained within the chamber when mixed with other gases. We set the concentrations of each gas at the same levels used in the mixed-gas tests($O_3$, $NO_2$, $SO_2$ = 0.3, 1.8 and 0.1 ppm, respectively). We then injected the gases and measured the concentrations within the chamber.

The following calibrated instruments were used for measurements:

- $O_3$: Automatically Adjusted Ozone Concentration Meter (OMR-5C), Suga Test Instruments Co., Ltd.
- $NO_2$; NOx-$NO_2$-NO Meter (42C), Thermo Electron Corporation
- $SO_2$:$SO_2$ Meter (43C),Thermo Electron Corporation

The results, shown in Table 1, revealed a loss of 70% in the $O_3$ concentration, compared with the set value. We also found that when the concentration of all gases was raised, the ratio of residual $O_3$ fell even further. Since $O_3$ has a high propensity towards oxidation, we believe that the mixing of $O_3$ at high concentrations with $NO_2$ or $SO_2$ makes it easier for reactions with these gases to occur.

**Table 1: Gas concentrations within the chamber during mixed-gas (O3:NO2:SO2=3:18:1) tests (Concentrations controlled prior to injection)**

| | | Condition 1 | Condition 2 | Condition 3 |
|---|---|---|---|---|
| Approx. concentration level compared with natural environment | | 100x | 330x | 3300x |
| | | | | |
| Before mixing (Set value) (ppm) | $O_3$ | 0.3 | 1 | 10 |
| | $NO_2$ | 1.8 | 6.3 | 63 |
| | $SO_2$ | 0.1 | 0.33 | 3.3 |
| | | | | |
| After mixing (Within chamber) (ppm) | $O_3$ | 0.09 | 0.15 | 0.09 |
| | $NO_2$ | 1.7 | 5.3 | 60 |
| | $SO_2$ | 0.09 | 0.31 | 3.3 |
| | | | | |
| Residual concentration (%) | $O_3$ | 30% | 15% | 1% |
| | $NO_2$ | Approx. 90% | | |
| | $SO_2$ | Approx. 95% | | |

### *Analysis of Reactive Agents Produced in the Mixed-Gas Tests*

In addition, we analyzed the ions ($NO_3^-$, $SO_4^{2-}$) produced in the samples exposed during the mixed-gas tests using ion-chromatographic analysis. In the samples exposed in the mixed-gas tests, compared with unexposed samples, we detected an amount of nitric acid ions that far exceeded the amount that is gradually produced during the actual indoor deterioration. Table 2 shows the concentration (ppm) of ions in aqueous solutions extracted from samples at 1ml/6cm$^2$. The estimated number of years of the mixed-gas tests was set at the same number indicated above, and the average $O_3$ concentration was calculated to be 4.6 ppb.

In addition, in the mixed-gas tests, the pH of the membrane of the exposed samples revealed a rapid drop that is virtually never observed during the actual indoor deterioration, even when compared with samples displayed for an equivalent number of years (Fig. 4).

**Table 2: Results of ion-chromatography analysis of samples exposed during accelerated mixed-gas tests and indoor display**

| | **Sample (Elapsed years)** | **$NO_3^-$ (ppm)** | **$SO_4^{2-}$ (ppm)** |
|---|---|---|---|
| Type | Unexposed sample | <0.1 | 0.6 |
| Mixed-gas tests | Exposed 2 d (equivalent to 4 M) | 47 | 0.2 |
| | 6 d (equivalent to 1 Y) | 85 | <0.1 |
| | 11 d (equivalent to 2 Y) | 129 | <0.1 |
| | 17 d (equivalent to 3 Y) | 135 | 0.2 |
| | 28 d (equivalent to 5 Y) | 153 | 0.1 |
| Natural elapsed time | 5 Y | 11 | 1.5 |
| | 10 Y | 30 | 1.2 |

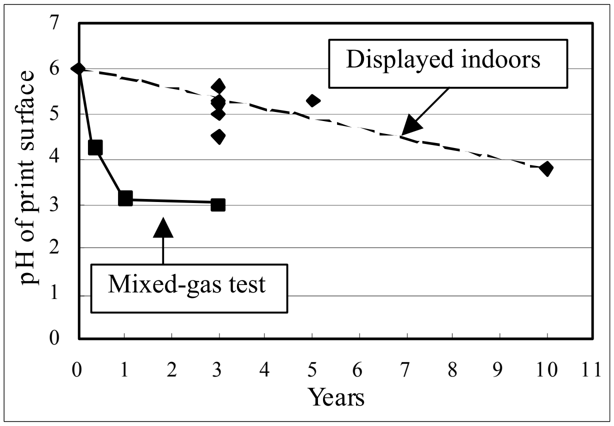

*Figure 4. Comparison of Surface pH between Samples Exposed to Accelerated Mixed-gas Tests and Samples Displayed Indoors.*

### *Considerations Regarding Mixed-Gas Tests*

In the mixed-gas tests, $O_3$, $NO_2$ and $SO_2$ are mixed at concentrations higher than those in the natural atmosphere; therefore, the reaction between the gases is rapid, producing nitric acid, which we believe produced a low pH environmental condition on the paper's surface which deviated over a short period of time from the behavior that occurs during the actual indoor display.

Due to the high concentration of $O_3$ compare to natural environment, we believe it is possible that the following reactions, for example, take place rapidly within the chamber.[7]

$$NO_2+O_3 \rightarrow NO_3+O_2 \quad (1)$$

$$NO_2+NO_3 \rightarrow N_2O_5 \quad (2)$$

$$N_2O_5+H_2O \rightarrow 2HNO_3 \quad (3)$$

As long as the gases are mixed at concentrations higher than those in the natural atmosphere, the suppression of such reactions may be difficult.

During the actual mixed-gas tests, the setup was such that the concentration of each gas was controlled within the chamber, and so it is possible to set the gas concentrations so they appear to conform with the set values. However, in actuality, the equipment automatically injects $O_3$ to compensate for the $O_3$ that is lost, further triggering the side reaction, making it impossible to accelerate the environmental condition that the test originally intended to reproduce.

As described above, since mixed-gas tests that include high concentrations of $O_3$ produce phenomena that differ from the phenomena produced during the actual indoor display, the results obtained from mixed-gas tests at the present time may be considered unsuitable for ranking the image stability of inkjet prints, or the prints produced with different image-formation technologies.

We recommend the adoption of single-gas tests using three gases, $O_3$, $NO_2$ and $SO_2$ respectively. We believe that $O_3$ gas test is essentially judged by the previous papers[1-3] relating to the correspondence between $O_3$ gas test and actual indoor fading. $NO_2$ gas test and $SO_2$ gas test are also indispensable because they sometimes reproduce fading phenomena which are occasionally observed especially in highly polluted air environment, such as in a room with kerosene heater.[3,4]

## Conclusion

Unlike single-gas $O_3$ tests, which approximates the image deterioration in the actual display, the same actual indoor deterioration is not reproduced in mixed-gas $O_3$, $NO_2$ and $SO_2$ tests, depending on the type of sample.

In mixed-gas tests of $O_3$, $NO_2$ and $SO_2$, due to the rapid reaction between the gases within the chamber, a rapid loss of $O_3$ concentration occurs, accompanied by a reaction that produces nitric acid. As a result, the nitric acid gives rise to a low pH environmental condition on the surface of the samples, which deviates from the behavior that occurs during the actual indoor display.

Because the problems described above occur in mixed-gas tests using $O_3$, $NO_2$ and $SO_2$ at concentrations higher than those in the natural atmosphere containing $O_3$, we intend to study the evaluation of gas resistance using independent single-gas tests of $O_3$, $NO_2$ and $SO_2$.

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## Author Biography

*Yukihiko Kanazawa received his master's degree in engineering from Osaka University in Japan in 1984. Since then, he has worked in the Ashigara Research laboratory at Fuji Photo Film Co.,Ltd in Japan. His work has focused primarily on the development and evaluation of imaging materials and related areas.*