Image Stability of Ink Jet Prints: Investigations on the Impact of Ozone

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Abstract

Ever since the quality of ink jet prints and ink jet photographic prints reached a high level, the gas fading of dyes has become a more important issue. But so far a standardized test method for gas fading does not exist. Since it is believed that ozone has the most impact on the gas fading phenomenon, a testing system was developed which studies the effect of ozone exposure on ink jet prints.

Since humidity plays a significant role in the fading effects of ozone, it is very important to guarantee a constant humidity level during testing.

Introduction

Ozone is known as a very aggressive substance and it belongs to the most powerful known oxidants.[1] It is able to oxidize all metals to their highest oxidation levels. The only exceptions are gold, iridium and platinum. Carbon and many organic compounds like ethers, alcohols and fats combust in the presence of ozone. So it is not surprising that ozone also attacks the molecules of colorants, in particular dyes. In organic synthesis it is often used in diluted form to give aldehydes, ketones, carboxylic acids, etc. by a controlled oxidation reaction.[2] Ozone is also well-known as the protecting principle for UV radiation from the sun. In the stratosphere it adsorbs the ultraviolet radiation near the wavelength of 255 nm to convert it into relatively harmless IR radiation.

Nevertheless ozone plays a role as a toxic substance. According to WHO[3] the average exposure time for humans over 8 hours should not exceed a value of 0.05 to 0.06 ppm (100–120 µg/m^3).

Ozone and Ink Jet Prints

In most countries the ozone concentration normally rises during summertime up to noticeable concentrations. Furthermore ordinary office machines like laser printers, copiers and UV lamps are sources for ozone. The resulting concentrations of ozone are sufficient to affect colorants, for example, on ink jet prints. The phenomenon of gas fading has long been recognized as an important aspect of traditional dye applications like textiles and it is believed to be mainly caused by ozone.[4] Recently the effect becomes an issue for ink jet prints, especially when they are made on microporous paper, which reinforces the impact of ozone.

Many investigations were done to understand the mechanism of the ozone oxidation of organic compounds, in particular dyes. Generally it can be observed that if the electron density in a organic molecule is increased a higher ozone sensitivity can occur.[5]

This behavior is measurable by the Hammett Equation. It is also known that a metal complex in a dye molecule affects the fastness properties especially the light fastness. But unfortunately it has to be considered that light fastness and ozone fastness do not always correlate. Direct Blue 199, for example, is well-known for its excellent light fastness, but the ozone fastness is rather poor.

In the technical literature many descriptions are found for the mechanism of ozone oxidation. Basically ozone itself or the decomposition product singlet oxygen is believed to be the active species in the oxidation process of organic compounds.[6]

Other pollution gases like NO_x and SO_2 are also considered to be aggressive agents, but they seem to play only a minor role in the gas fading phenomenon of colorants.[7]

Ozone Test Equipment

For the investigation of ozone fastness of colorants it is crucial to use a monitoring system, which allows the treatment of ink jet prints with ozone under definite conditions. For this purpose ozone test equipment was developed. An ozone generator produces the ozone by silent arc discharge and the ozone concentration can be obtained in a broad range from 1 to 100 ppm.

For ozone treatment the samples are put in a transparent chamber. A regulating system in connection with a UV photometer as an ozone detecting device keeps the ozone concentration at the desired level. For safety reasons the ozone is destroyed after leaving the test chamber. Therefore the ozone containing air is pumped through a container with activated charcoal and afterwards pure air leaves the closed circuit of the test system.

For a homogenous distribution of the ozone inside the test chamber, the use of a small conventional fan is recommended. It is advisable to prevent the airstream from flowing directly on the test samples.

Besides a constant ozone concentration, a constant temperature and a definite relative humidity are also essential during the testing. Normally the ozone tests are carried out at standard laboratory conditions at 20-24°C. Depending on the location, season and weather conditions the relative humidity can vary in a broad range (20-90%). Trials with dyes at different levels of relative humidity have proved that increased relative humidity significantly reinforces the impact of ozone. Therefore a constant humidity helps to guarantee the reproducibility of test data. A convenient method to achieve a constant level of relative humidity uses a concentrated salt solution in the test chamber. With different types of saturated solutions of inorganic salts it is possible to fix nearly every level of relative humidity.[8] A saturated sodium chloride solution leads to a rather high level of relative humidity (70-74%). Alternatively solutions of magnesium nitrate (52-54% R.H.) or potassium carbonate (40-43% R.H.) can be employed.

After the ozone treatment the color change of the sample is measured. The residual optical density gives a quantitative assessment of the dye fading. It is a suitable method but only if shift in hue is negligible. The CIELAB Colorimetry ΔE evaluates even small color differences and should be employed if changes in hue are an issue. The coloristic measurements can be carried out by a standard spectrophotometer.

Before a sample is tested in the ozone chamber it must be considered whether more or less rigid conditions should be applied. Prints made with sensitive dyes on microporous paper need only low concentrations of ozone (at low relative humidity) compared with prints with yellow or pigmented ink jet inks, in order to get reasonable effects of colorant decomposition.

The chart below makes that point. Samples of ink jet prints were made with standard dye-based cyan, yellow, magenta and black inks with an HP 5000 printer on Epson Premium Glossy Photo Paper. Afterwards the prints were treated with 10 ppm ozone for 10-40 minutes (72% R.H., 22°C).

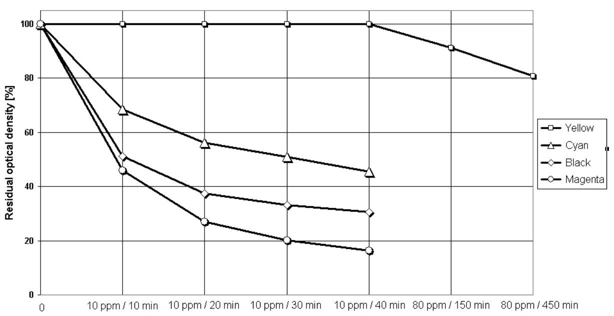

Figure 1. Ink jet prints after treatment with ozone

The cyan, a copper phthalocyanine dye, the magenta and the black already show a rather strong color fading even at the moderate conditions due to the microporous structure of the paper. Only the yellow samples were held at 80 ppm for an additional 150-450 minutes in order to obtain a significant color fading. In general yellow dyes used in ink jet inks are azo dyes and most of them are usually highly ozone resistant. By using other kinds of ink jet papers i.e., swellable paper, the impact of ozone on the dyes comes less distinctive.

Strategy for Better Ozone Fastness

In recent years many efforts were made to improve the properties of ink jet prints. Therefore it is a key issue to achieve less ozone susceptibility especially when high quality must be obtained in photographic printings. Some general methods are mentioned:

- Inks made of dyes with higher ozone fastness
  - Suitable chemical structures may prevent the destructive reaction of ozone with the dye molecule
- Pigment based inks
- Specially designed ink jet papers
- Additives used in inks and paper layers
  - substances are preferably consumed by ozone instead of the dye
  - Radical scavengers
- Coating processes like lamination
- UV curing techniques

Conclusion

Ozone obviously plays the major role in gas fading pheno-mena. Suitable equipment for measuring the impact of ozone is an important tool to develop strategies for improved ink jet prints. For the sake of reproducibility, the main factors like ozone concentration, temperature and relative humidity have to considered. Ozone testing equipment was tailor-made for laboratory purposes to meet these demands.

References

1. Römpp, Lexikon Chemie (10.Aufl.), Georg Thieme Verlag, Stuttgart.
2. Bailey, "Ozonation in Organic Chemistry," 2 vol, Academic Press, New York 1978, 1982.
3. Air Quality Guidelines for Europe, Kopenhagen: WHO 1987.
4. Salvin, Journal of the American Dyestuff Reporter, Vol. 49, 12, 1964.
5. Pryor, Giamalva, Church, J. Am. Chem. Soc. **105**, 6858, 1983.
6. Gorman, Rodgers, Chem. Soc. Rev. **10**, 205, 1981.
7. Kitamura, Hayashi, Oki, International Congress of Imaging Science, Tokyo, **539**, 2002.
8. Handbook of Chemistry and Physics, CRC Press 1995.

Biography

Klaus Saitmacher received his Ph.D. degree in organic chemistry from the Friedrich-Wilhelms University in Bonn / Germany in 1989. He began his career in the textile dye business unit at the former Hoechst AG in Frankfurt. In 1998 he joined the Clariant GmbH Division Pigments & Additives at Industrie Park Höchst, Germany. He worked on the development of azo pigments and was in charge of production quality. Now in Clariant's Non Impact Printing group he primarily focuses his project activities on the development of colorants for ink jet applications.