

Features of Reciprocity Failure and Ozone Fading in Ink Jet images

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Why Ozone Fading is Important

This paper discusses the background to ozone fading on porous media and points the way to reliable testing methods. Firstly the amount of ozone, indoors and outdoors is investigated, using data from a wide variety of sources.

Secondly, we compare forced air flow methods with chambers using raised ozone levels and the main features of each method outlined. We also briefly examine the possible role of other pollutants and synergy between light and ozone in fading of images – evidence for these being important is so far weak.

Finally we look at ways of understanding the basic chemical processes.

Introduction

Pollutants are known to have a major impact on the permanence of ink jet prints printed on porous media (Ref 1). In many cases, the degradation due to low levels of ambient ozone pollution can be much faster than that due to typical light levels.

In order to solve these problems we first need to understand their source, and be able to quantify their extent. In this paper then, we summarize the data for how much pollution typical ink jet prints are likely to be exposed to, and describe some test methods for examining the process, with their respective advantages and disadvantages, and show some of the remaining issues to be considered before reliable predictions can be made. We also examine some of the more important features of the phenomena, and show our approach to understanding the underlying mechanisms.

Outdoor Ozone

We started with ozone since it appears to be the most important pollutant in this phenomena for various reason (see later). Background levels of ozone in clean air are typically 10ppb. In polluted air this can rise to over 100ppb averaged over an 8 hour period. Much data has been collected on ozone levels in industrialised countries due to its adverse effects on human health, but generally this has been to with a viewing to assessing the peak concentrations; human health is not seriously affected at lower concentrations.

For our purposes however, we are more interested in average concentrations over long periods (years). We have therefore collected large amounts of real time ozone data for as many geographical areas as possible. In the UK there are approximately 70 automated monitoring stations that report the concentrations of various pollutants every 15 minutes. It is important to examine data for the entire time period 24-hour day, 365-day year. Many monitoring stations in some countries are only operated during the ozone season, or during the day. We have taken this data for all the stations over the last 5 years and this provides us with a very large data set and gives clear pictures of geographical and temporal variations.

Average outdoor ozone concentrations in the UK over this period were 20ppb. Clear seasonal cycles are seen (eg Fig. 1), with early summer in the UK giving the highest concentrations, dropping to approximately half their summer maximums in winter. In addition it is clearly seen that urban areas have lower ozone levels than suburban or rural areas. This is explained by the fact that ozone is a secondary pollutant and can react with primary pollutants, thus reducing its concentration in areas close by the source of the primary pollution. (eg NO reacts with ozone to produce NO₂ and O₂, at lower concentrations of NO, the photochemical generation of O₃ dominates)

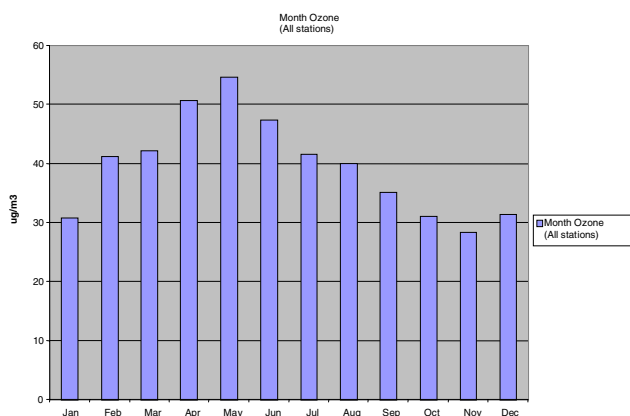


Figure 1.

Ozone concentrations for various other developed countries follow a similar pattern. Whilst there are geographical variations in concentrations and significant spikes over short time periods it should be emphasised that over long time periods (years), the range of observed outdoor ozone concentrations falls in a rather narrow range 20-50ppb.

We should be encouraged by this, since it should make predictions (when we come to make them) relatively accurate compared to predictions of say lifetime due to light exposure. This is because real display conditions for light varies enormously in intensity (<100lux->10klux).

Indoor Ozone

Indoor ozone has been less studied but there is still a good deal of information available (Ref 2). The key point to remember when considering indoor ozone concentrations is that ozone is reactive, and reacts readily with surfaces inside buildings. The half-life for ozone in a number of containers has been measured as only a few minutes.

Indoor ozone closely follows the outdoor concentrations – which is by far the most significant source of indoor ozone. The reactivity of ozone with various surfaces has been quantified, and the flux rates across these surfaces estimated. The most important factors controlling the indoor/outdoor ratio are the rate of air exchange with the outside air, and the surfaces present in the building, e.g. textile surfaces are generally more reactive and act to reduce the steady state ozone concentration from any given outdoor ozone concentration and exchange rate. The reactivity of a number of surfaces has been determined.

Other factors that are important is the presence and type of any air conditioning. The indoor/outdoor ratios for a wide variety of scenarios have been measured and a number of general conclusions can be drawn about what situations we might expect ozone fading to occur more easily in.

For example, residential buildings typically have lower indoor/outdoor ratios because they have more soft furnishing and less ventilation. Public buildings such as schools, hospitals, museums etc. have higher ratios because they have more hard surfaces and/or are more ventilated.

Test Methods

The two main test methods so far used have been “forced air flow”, and chambers making use of controlled raised ozone concentrations. In the forced air test, ambient lab air is simply passed over the samples at a convenient rate and the samples response is monitored. The advantages of this technique include cost (it is very cheap to do); all the data for the fading of the image is available, as opposed to a single point measurement; a full “cocktail” of pollutants is used rather than any one in isolation. Disadvantages are that it is more difficult to control the humidity or temperature, and impossible to control the level of pollutants. This can be dealt with by including a control sample and always fading the control to a particular set point. The method can also be

slow (>60 days), and so unproductive. We also have to ask what is happening in this experiment, and it is likely that increasing the flow rate improves the mass transfer, by replenishing the used ozone from the surface. If this is so then this system is limited to accelerating those systems that are so reactive that they are diffusion controlled. More ozonefast dyes may not be accelerated by this method because they are not limited by the rate of passive diffusion of ozone to the sample. It could therefore take a long time to collect data for very ozonefast samples.

The raised ozone chamber method has advantages of control of ozone level, humidity and temperature, and being more productive and faster for longer term testing. It is however much more costly to acquire. The air/ozone flow over samples in our equipment is designed according various test criteria (ISO 1431-1 and 2, BS903 etc.), and our early experiments indicate that this gives the non-diffusion controlled measurements. Much work remains to be done to confirm this and also to show how these measurements can be related to “real life” exposures for samples that are subject to diffusion limits.

Using the forced air flow method we have looked for synergistic effects between light and ozone. This is achieved by a chamber with twin shelves, with the upper shelf being illuminated (600lux). Over the course of 90 days, we did not observe a significant difference between the fade rates of samples on the upper shelf (illuminated & air flow) and lower shelf (air flow only). However it would be useful to check this further for uv sensitivity and other chromophores.

Other Pollutants

It is well known that other pollutants are present (from our characterization of pollutant levels), and also that these can have an effect of colourants. In particular it is known that certain anthraquinone blue dyes can react readily with NOx to give red dyes. We have therefore tested a number of chromophores on a number of media (swellable and porous types) under standard test method conditions, as specified by ISO 105-G01 and G02.

The results for these showed an entirely different signature to the experiments with ozone. Shade changes and OD losses were observed but in general these were much less than with ozone, and often very different in type. Nor did the other pollutants (NOx and Burnt Gas Fumes) agree with publicised reports from end users (loss of OD in cyan and black becoming orange brown). We therefore concluded that at least for the systems we have studied so far, other pollutants were less important than ozone, but that they should not be neglected.

Understanding the Chemical Mechanisms

In order to properly solve the problem it is necessary to have a reasonable understanding of both the physical and organic chemistry involved in the degradation of colourants by ozone. There are numerous approaches to this, the most

obvious being isolation of degradation fragments from printed media after exposure in our ozone chamber. This can be quite difficult and time consuming to analyze but we have done it for a number of cases.

Possibly a more useful approach it to start with the solution study method, and for this we have built a custom ozone degradation apparatus (fig 2). This allows us to study in some detail the mechanism and kinetics of the reaction of colourants in aqueous solutions, from the first initial attack through to final products, by sampling the reaction mixture and analyzing by HPLC, HPLC-MS, nmr, uv-vis etc. The dominant degradation mechanism for one chromophore we have studied is shown below – although a number of other products have also been identified. Additional work has shown that the solution chemistry does give a good model of the processes happening on porous substrates both in terms of its relative kinetics and the products observed.

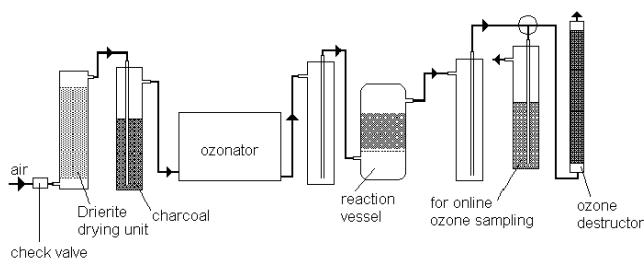
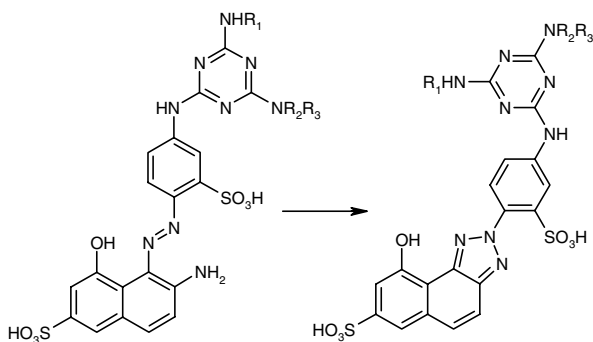


Figure 2. Apparatus used for study of solution ozonolysis



Scheme 1. Orthoazo amino compounds are easily oxidized by ozone to a naphthotriazole.

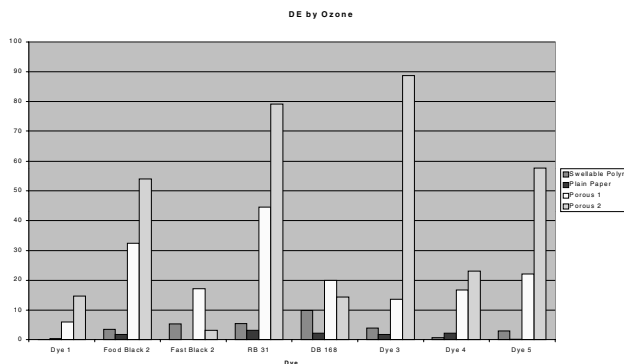


Figure 3. The range of reactivities observed towards ozone is large.

Solving the Problem

Using the above tests and techniques we have been able to understand much more about this process and begun to synthesise much more resistant colourants. As we would expect from chemical kinetics, in the selective reaction of ozone with organic molecules the range of reactivities is very high, allowing us to make much more resistant compounds (50-100x less reactive). Again, this encourages us to believe that there are solutions to this problem.

References

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2. Weschler CJ, *JACPA*, **39**(12), 1562-8

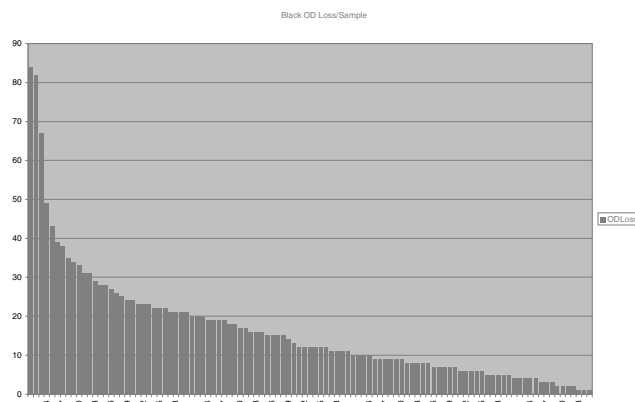


Figure 4. Range of reactivities observed for black samples

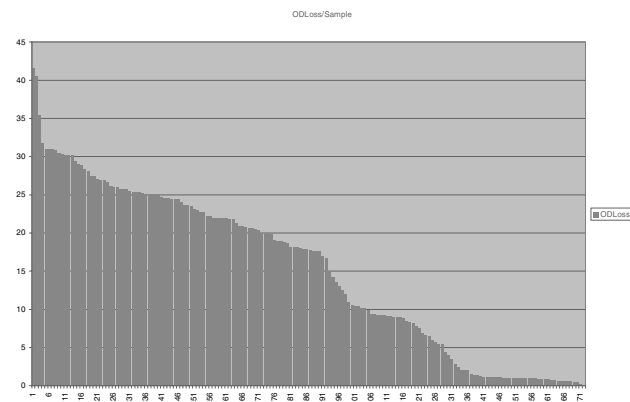


Figure 5. Range of reactivities observed for cyan samples

Biography

Paul Wight received his B.Sc from Durham University, UK in 1986, and a Ph.D. in organic chemistry from Nottingham University (UK) in 1990. He started work for the then ICI, on novel chromophores and disperse dyes. After 5 years he joined the ink jet research group, and has worked on a wide range of projects as the company reincarnated itself as Zeneca and now Avecia. He currently leads a team titled "Fundamental Understanding" using a combination of physical chemistry techniques, analysis and synthesis, with the objective of discovering useful new science underlying ink jet chemistry and processes.