Developing Pigmented Inks for Office Printers

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Formulabs Ibérica´s know how in the chemistry of colour is based on over 60 years experience, being first in the fields of formulating pastes and varnishes for the colour lead pencil industry, ribbon inks and carbon paper pastes. Since 1979 the Company is active in the fields of writing instrument inks and industrial inks for colouring and coding purposes in the wire, cable and optical fibre industry.

More recently, since 1987, Formulabs Ibérica is holding a pioneering position in the development of inkjet Inks in the market, providing inks for the most sophisticated desktop printers and graphic arts inkjet (wide format) printers under the Formujet brand.

Formulabs Ibérica´s Chief Inkjet Inks R&D manager, Ph.D. Dr Ramón Casas submits following article.

We are becoming accustomed to constantly seeing new printers that use pigmented black ink cartridges on the market. Hewlett Packard* launched their 1200 printer with the 51640 cartridge including pigmented black ink a long time ago. Since then, new generations of cartridges and inks have appeared as a result of attempts to manufacture an ever more perfect product.

It is debatable whether or not the end user really needs black pigmented ink for office printers, and whether or not it is practical to have a printer with a light resistant pigmented black and dye based inks that are scarcely light resistance, but that is not the concern of this article.

However, there is certainly a demand for such products that must be met by ink manufacturers.

The quality and stability of pigmented inks depend on factors, that are very different from those usually discussed in relation to dye-based inks. There is still series of factors connected with the pigment structure itself that differentiate it from a dye. Conceptually, a pigment is a solid particle with a quantifiable physical dimension, (volume, diameter, etc.), that disperses throughout the medium rather than dissolving within it. Dyes are soluble in suitable solvents: they dissolve, and do not therefore contain solid particles. Each dye molecule is solvated. In the case of a formula for a pigmented ink, there is a series of additives on the market that facilitate the process of wetting the pigment by forming a film around the particles. In short, the above mentioned additives work as linkers between the dispersing medium, and the solid particle in suspension.

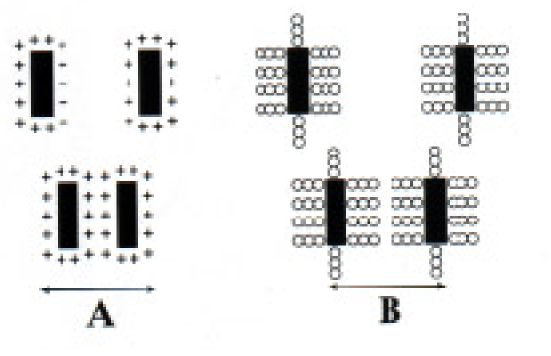

Figure 1

The most common black pigment is Carbon Black - that is, finely divided carbon agglomerates. The basic characteristic of this pigment is its light-resistance and its low dispersability in polar media, such as water. For this reason, manufacturers of Carbon Black have developed a special technique to prepare the surface of these particles in order to create points of co-ordination between the pigment and the aqueous medium that surrounds it. These points of co-ordination permit the "fixing", or co-ordination, of the pigment with the wetting agent, which facilitates the particles dispersion in the water, and also stabilises the product against thermodynamically inevitable processes such as flocculation and sedimentation. The anti-flocculating and anti-settling agents basically function as shown in the two methods represented in **figure 1**: the electrostatic and the esterical repulsion methods. The **electrostatic repulsion method (figure 1, A)** is based on the principle that two particles charged with the same kind of charge repel each other, and the **esterical repulsion method (figure 1, B)** is based on the principle that the centre of two large elements may not come together because they have an outer layer which prevents this from happening.1

Having described the different stabilisation methods, we must now examine the control methods for a pigmented ink in order to quantify its invariability over time during the ageing process. Everyday experience shows that the best test for determining the properties ascribed to any product, and particularly to an ink, is by measuring them in real time (Real Ageing Test). However, current technology is developing so rapidly that scientists must develop accelerated methods to simulate what nature would do in real time (Accelerated Ageing Test). All of the methods scientifically designed to study product ageing are rationally based. Knowledge of chemical kinetics is generally used to look for equivalence between Real Ageing Test and the Accelerated Ageing Test. Chemical Kinetics describes the factors on which reaction speed depends by means of equations: product concentration and temperature **(Equation 1)**. For a specific ink formula, the product concentration is fixed and therefore is not a variable that can be modified to accelerate the speed of the reaction or process. The only variable that permits rational intervention is temperature **(Equation 2)**. The influence of temperature on reaction speed is expressed by:

$V = k [A]a[B]b$ ... Speed Equation **(Equation 1)**.

$k = A0e-Ea/RT$ Arrhenius Equation **(Equation 2)**.

Where [A] and [B] are the product concentrations, k is the reaction speed constant (if k is double, the speed of the process is double), A0 is a constant that is characteristic of the process and is known as the pre-exponential or Arrhenius factor, Ea is a constant characteristic of the process, and is known as Arrhenius activation energy, and R is the gas constant. It is clear that, everything described so far is constant, and therefore cannot be modified by the researcher, but intervention is possible in the case of the only variable in the equation: temperature. In general, it can be said that for every 10ºC increase in temperature, the reaction constant k, and therefore the speed of the process, doubles or triples (depending on the process). The reverse reading of the same **Equation 2**, reveals that the speed of a physio-chemical process will be 2 Ð 3 times faster with every increase of 10ºC.2

With regard the study to quantify the stability of pigmented black ink for InkJet application, we have developed the following method:

The particle size distribution of the pigmented ink was checked at the time of manufacture, and variation over time was monitored in an accelerated ageing test. The test temperature was fixed at 60ºC, which represents 4 increases of 10ºC, with respect to real conditions of 20ºC. These four 10ºC increases mean that the variation observed in a measurement carried out after one month at 60ºC would theoretically be the same as the same measurement after a Real Ageing Test at 20ºC for 16 months (24 under the worst possible conditions), in accordance with the Arrhenius equation described above.

Figure 2

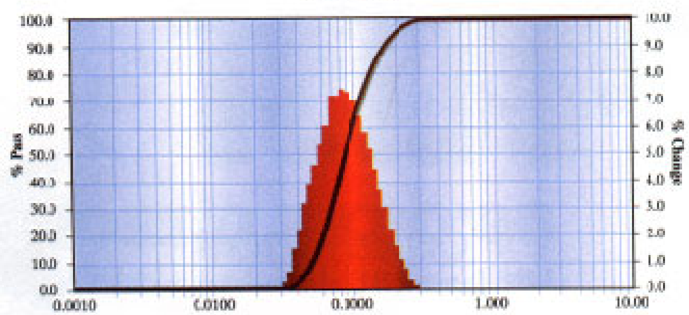

Figure 3

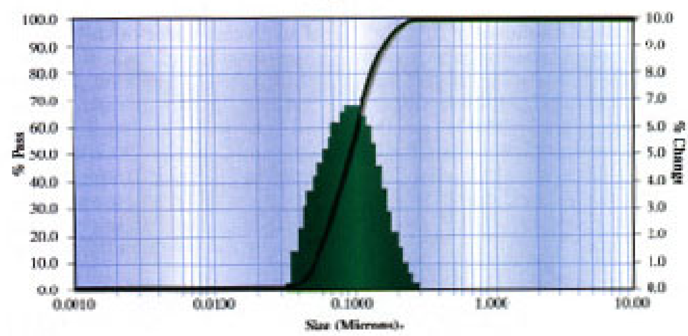

Figure 4

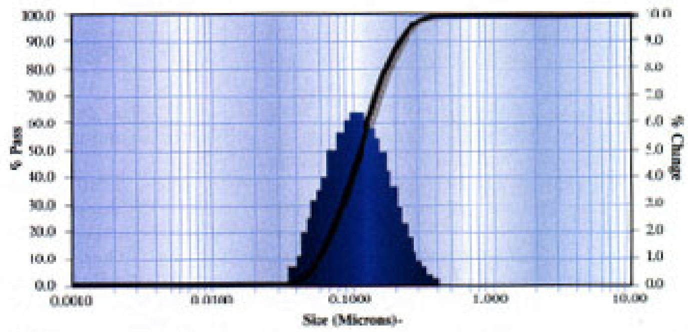

Figure 5

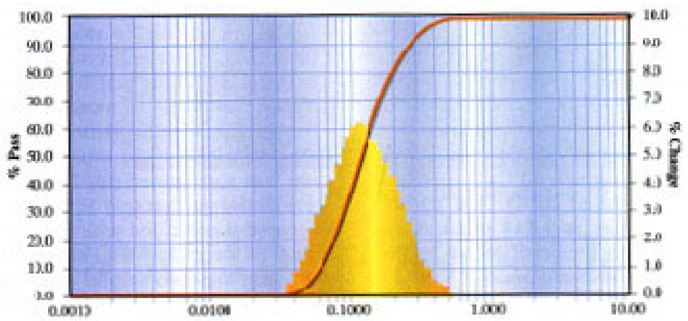

Figure 2, 3, 4 and 5

Thus the results obtained in the study of a pigmented black ink suitable for the recycling of Hewlett Packard* 51629 A and 51645 A cartridges are reflected in **figures 2, 3, 4 and 5. Figure 2** shows the results of the analysis of the ink when recently manufactured, where the particle maximum is 0.0859 microns and 100% of the particles are smaller than 0.2891 microns. **Figure 3** represents the analysis carried out after 2 weeks at 60ºC (8 months in real time at 20ºC), where the particle maximum is 0.1114 microns and 100% of the particles are smaller than 0.2891 microns. **Figure 4** shows the analysis after 4 weeks at 60ºC (16 months in real time at 20ºC), where the particle maximum is 0.114 microns and 100% of the particles are smaller than 0.4088 microns. Finally, **Figure 5** represents the analysis carried out after 8 weeks at 60ºC (2 years at 20ºC), where the particle maximum is 0.1215 microns and 100% of the particles are smaller than 0.5781 microns. All these results are featured in **Table 1.**

Figure	Temperature (ºC)	Time (weeks)	Micron max.	Micron 100%
2	Initial	Initial	0.0859	0.2891
3	60	2	0.1114	0.2981
4	60	4	0.1140	0.4088
5	60	8	0.1215	0.5781

Table 1

The results of this Accelerated Ageing Test are very promising. The increase in particle size is carefully controlled, and is totally acceptable for InkJet application for a period of two years under the test conditions described (20ºC). It is forecast that after this period, the ratio between the largest particles detected in the ink and the injector is approximately 1:50. What does this mean? To offer an analogy, we could say that the probability of this pigmented ink blocking an InkJet injector is the same as that of a pea (5 mm diameter) blocking a medieval cannon (25 cm diameter). The assurance offered by this control carried out by means of an Accelerated Ageing Test might be disputed by the more incredulous or demanding. Therefore it should be added that a Real Ageing Test was carried out together with the accelerated one, at standard room temperature (25ºC). This test consisted of recycling Hewlett Packard* 51645 A cartridges with the compatible pigmented ink that was the object of this study, and no variation in print quality was observed in the case of cartridges that had lain unused for 10 months. The startability of these cartridges at the time of testing was also immediate. This test was only carried out over 10 months, because it coincided with the creation of the pigmented formula. It is hoped that in 6 months time, it will be possible to extend these data over a 16-month period.

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