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High electrical conductivity waterborne dispersions of carbon black pigment

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Abstract

The carbon black grades that are employed as pigments in printing inks are characterised by low surface area, low structure and a higher proportion of chemisorbed polar groups on the surface. All of these features render the pigment easily dispersable – a property crucially important in the case of printing inks. However, high electrical conductivity of carbon black is known to be possessed only by the grades that have high surface area, high structure and lower proportion of polar groups, and consequently poor dispersability. The study reported here aimed to resolve such a dilemma between high electrical conductivity and poor dispersability. Thus, novel methodologies were developed to prepare waterborne, binder-free dispersions based on "non-printing ink" grades of carbon black, followed by a separate letdown stage and subsequent testing stage that is reported in Part B of this paper. The particle size analysis, rheological characterisation, sedimentation analyses and electrical characterisation results clearly indicate that the selected pigment grades of carbon black were successfully stabilised as dispersions that possess high electrical conductivity at considerably lower pigment loadings than normal.

1. Introduction

As new applications of printing inks are envisaged, increasing numbers of pigments are employed as functional materials in inks [1-2]. These functional pigments impart different functionalities to printing inks, including electrical conductivity [3-11], magnetism [12-14], and so on. To produce printing inks that possess electrical functionality, metals such as gold, silver, copper and nickel can be used [15-18]. Non-metallic conductive materials such as carbon (carbon black , carbon nanotubes [10], graphite/graphene [19-20], fullerenes, etc.), some metallic oxides [21-22], conductive polymers [23-24], conductive ceramics [25] and so on, can also be incorporated into the ink formulation to achieve various levels of electrical conductivity, often lower than those that can be achieved with metal dopants.

Carbon black, when used as a conductive pigment in an ink formulation, has certain advantages over other conductive fillers. These advantages include, but are not limited to, the relatively lower cost, the option of adjusting the conductivity in a broad range and the retention of flexibility and other desired mechanical properties of the final ink film. In an essentially insulating matrix, such as an ink, electrical conductivity is dependent on the carrier medium, the type, the loading and the distribution of the conductive filler during and after the application of the ink. Conductivity is observed because of the formation of a continuous path for the flow of electrons. This continuous path is referred to as the percolation network [26]. In the case of carbon black, the formation of the percolation network is governed primarily by the quantity of carbon black which, in turn, depends on the morphology of carbon black [27]. Any structural feature, such as porosity, which increases the specific volume of pigment, will also increase the possibility of closer contact between the adjacent carbon units [28]. The major features having a significant effect on properties of a carbon black such as the blackness, the dispersibility and the electrical conductivity, are the particle size, the structure and the surface chemistry [29-30].

The smaller the carbonised droplets or nodules that comprise the carbon black aggregates are, the tighter is the packing ability of the aggregates. Tighter packing results in smaller gaps between the conductive carbon units and a closer resemblance to a continuous conductive medium. This point is especially important for good conductivity to be achieved.

Low-structure carbon blacks allow greater pigment loadings to be used and impart greater gloss because of their lower vehicle demand. Low-structure blacks have less occluded air and, thus, are easier to wet-out than are the high-structure blacks. However, because of the closer packing of the aggregates, they are more difficult to disperse [31]. At a given weight loading, the probability of closer contact between the adjacent carbon black aggregates increases with an increase in the structure of the carbon black aggregates. It is believed that for good conductivity, the adjacent carbon black aggregates must be within about 5 nm, so that electron transfer by tunnelling mechanisms can occur [32].

Carbon blacks of the same particle morphology may vary considerably in their ease of dispersion. Such differences in dispersibility can be attributed to the amount of chemisorbed complexes which, in turn, depends on the manufacturing method and on the raw materials used [33-34]. It is known that the oxygen on the surface of a carbon black particle influences the technical use of this material more than does any other type of chemisorbed complex [35]. The polar chemisorbed oxygen sources increase the wettability of the carbon black surface by polar solvents and resin precursors. The increased wettability results in the better and faster dispersion of the carbon black in a polar dispersion medium [36-37]. While it is generally desired by the coating/ink producer, a high volatile content increases the surface resistivity because the oxygen-containing fractions act as electron scavengers on the surface of the carbon black aggregates. The increase in volatile content creates a dramatic decrease in the electrical conductivity for both the large surface area/high structure grades and for the small surface area/low structure grades of carbon black [33].

Abundant literature is available on the use of carbon black in printing inks for textile and non-textile applications [38]. However, the current study has a focus on waterborne, electrically conductive inks that were formulated using the non-printing ink grades of carbon black, including the very high surface area grades which are generally considered unfit for such applications. Specifically, the utility of such carbon black-containing inks in the context of textile printing was investigated. Aqueous binder-free pigment dispersions were produced in the first phase of this study. The following characteristics were considered to be the necessary properties of the pigment dispersions.

- High pigment loading.
- Low viscosity for easy incorporation of binder during the let-down stage.

- Good storage stability without pigment sedimentation or increase in viscosity.
- Excellent compatibility with the let-down binders being used. This means that no re-flocculation should occur during or after let-down with binder.
- High electrical conductivity.

In the second phase of this study, the formulated carbon black dispersions were converted into finished inks for textile printing followed by performance testing of these inks. This second phase is reported in Part B of this paper.

2. Materials

Pigments

On the basis of a consideration of the properties, electrically conductive grades of carbon black pigment that contained low volatile matter content were selected for the preparation of binder-free, waterborne dispersions. Two low surface area and two very high surface area grades were selected in order to establish that the dispersion preparation procedure that was devised in this study can be successfully employed to produce stabilised (optimised) dispersions of these difficult-to-disperse grades of carbon black pigment. Data related to the main characteristics, as provided by the suppliers of the selected carbon black pigments, are shown in Table 1. Throughout this document, these commercial pigments are referred to as Carbon1, Carbon2 and so on.

Table 1: Specifications of carbon black pigments (as provided by the suppliers)

Pigment (Code*)	**Supplier**	**BET Surface area (m^2/g)**	**Volatile content (%)**
Vulcan XC605 (Carbon1)	Cabot	59	< 0.1
Ensaco 250G (Carbon2)	Timcal	62	0.2
Ensaco 350G (Carbon3)	Timcal	840	0.3
Printex XE2B (Carbon4)	Orion Engineered Carbons	1000	< 0.1

Dispersing additives

Three different dispersants, selected on the basis of their supplier recommendations for the intended application, were used to prepare stable dispersions of a pigment. The dispersants possess a hydrophobic backbone (that could be for example, polyurethane, styrene-acrylic, etc.) and hydrophilic steric stabilising chains that are usually based on alkoxylate chemistry (based on for example, polymers of ethylene oxide or propylene oxide). The hydrophobic backbone is grafted with hydrophilic stabilising chains resulting in a comb-type molecular structure. Thus, in aqueous media, these dispersants attach to the pigment due to the hydrophobic nature of the molecule's backbone.

The more important characteristics of the selected dispersants are provided in Table 2. Throughout the discussion, the dispersants are referred to as Dispersant1, Dispersant2 and Dispersant3, instead of using the commercial names.

Table 2: Dispersants used and their characteristics (as provided by the suppliers)

Dispersant (Code)	**Description**	**Density (g/cm^3)**	**Water solubility**	**Active Matter %**
Solsperse 44000 (Dispersant1)	Not disclosed	1.67	Soluble	50
BYK-190 (Dispersant2)	Solution of a high molecular weight block copolymer with pigment affinic groups	1.06	Completely miscible	40
Tego Dispers 760W (Dispersant3)	Aqueous preparation of surface active polymers	1.03	> 500 g/L	35

Defoamer

The generation of a foam, due to the presence of surface active compounds such as dispersants, is possible specially in waterborne pigment dispersions. This problem becomes more pronounced when a large amount of a dispersant is present [39]. Air bubbles can act as shock absorbers for the energy that is provided to break the pigment particle assemblies, during pigment dispersion process. Thus, one of the more important ingredients of a pigment dispersion is a defoamer or an anti-foaming additive [40]. Tego Foamex 805, which is described by the supplier as a modified poly-siloxane defoamer, was used in the preparation of pigment dispersions.

Substrate

Iggesund Incada Exel packaging paperboard, having a weight per unit area of 240 g/m^2 and thickness of 400 µm, was used as the substrate for electrical characterisation of the formulated pigment dispersions. The substrate is coated with a calcium carbonate clay to make the surface smooth and to absorb the printing ink uniformly in demanding processes such as half tone gravure printing and offset lithography. Thus, this substrate was considered to be suitable for electrical characterisation of pigment dispersions and printing inks. This is because in these experiments, it was crucial to minimise any variations in the electrical conductivity of the deposited dispersion/ink layer, which might be caused by substrate surface roughness and/or non-uniform absorption.

3. Methods

3.1 Dispersion optimisation process

In this study, waterborne dispersions of four different carbon black pigments were prepared using three different dispersants. Thus, twelve pigment-dispersant combinations were prepared and tested. The procedure adopted in this study was closely related to the ‘minimum viscosity method’ for the optimisation of pigment dispersions. A major limitation of the minimum viscosity method is that it can give lower estimates of the optimum dispersant dosage [41]. In the present study, one of the major characteristics of interest was the electrical conductivity of the pigment dispersions. Thus, 100% coverage of the pigment surface by the dispersant molecules was not targeted and dispersions which remained stable for up to four weeks were considered to be sufficiently stable. Furthermore, the optimum dispersant dosage was determined by preparing and analysing a ‘ladder series’ of dispersions containing dispersant amounts, calculated around the theoretical dispersant dosage [42]. To overcome the limitations of ‘minimum viscosity method’, rheological studies, sedimentation analysis, photoextinction studies and zeta potential measurements were carried out to characterise the optimised formulations of the binder-free pigment dispersions. A 4-step procedure, as described in detail in the following text, was devised to “optimise” the dispersions of the carbon black pigments.

A viscosity minimum is generally observed at the optimum dispersant dosage. This minimum has been shown to correspond to approximately 2 mg of dispersant for 1 m^2 of the pigment surface area as measured by the BET nitrogen adsorption number method [42]. Thus, in the first step of dispersion preparation, the theoretical amount of dispersant, referred to as 100% dispersant active matter on the weight of pigment (%DOWP) was calculated using the empirical formula given as Equation 1.

$$\%\text{DOWP} = \frac{BET\ surface\ area}{5} \quad \text{Equation 1}$$

The BET surface area (m^2/g of pigment), oil absorption number and other characteristics of a pigment can be used as tools to predict the maximum amount of pigment that can be dispersed provided effective calibration is carried out. However, it is important to note that aqueous media present greater challenges in the dispersion of non-polar carbon pigments and it is impossible to furnish an exact value of the maximum pigment loading in such formulations. Thus in Step 2 of the dispersion optimisation process, the maximum amount of pigment that could be dispersed using the theoretical %DOWP was determined. This was achieved by comparing the characteristics of ‘control’ pigment dispersion with a ladder series of dispersions. The control dispersion was prepared without a dispersing additive and the pigment dispersion was achieved with the aid of the Glascol HN2 acrylic resin. A ladder series of pigment dispersions was prepared such that each dispersion contained a known, specific amount of pigment and a corresponding theoretical %DOWP of dispersant, calculated as described in Step 1. The pigment dispersion possessing a similar viscosity profile to that of the control dispersion was selected for the next step.

In the third step, the optimum amount of dispersant was determined. This was achieved by preparing a series of pigment dispersions, each containing the maximum pigment amount, that was determined in the previous step, but different amounts of dispersant. Using the cumulative results from viscosity determination, particle size analysis, zeta potential measurements and electrical property characterisation, the dispersions that were prepared in Step 3 were compared and the optimum dispersant dosage was determined. The optimum dispersant dosage (%DOWP) was determined using only one of the dispersants, followed by the use of the optimised formulation to prepare pigment dispersions using the other two dispersants.

In Step 4, dispersions of a pigment were prepared using each of the three dispersants considered in the study. Since these dispersions were prepared using the optimum %DOWP, they are referred to as the ‘optimised dispersions’. The properties that were characterised to compare the different optimised dispersions of a pigment included the viscosity, the dispersion stability and the electrical conductivity. In this step, the pigment loading was maximised while maintaining the optimum pigment:dispersant ratio.

3.2 Bead milling

During pre-mixing, the dispersion was mixed at 800 RPM for 5 minutes followed by mixing at 2000 RPM for 25 minutes. This initial mixing at the lower speed is important to achieve a high level of pigment wetting and to prevent any compaction of pigment agglomerates. The compaction of agglomerates is possible if the pigment is subjected to strong impact forces when the pigment surface is not properly wetted-out.

To create improved dispersions, the pre-mixed dispersion of a pigment was bead milled. In this study, the bead mill was a Mini 50 Motormill (Model No: MK11.M50.VSE.EXD.DI), manufactured by Eiger Torrance Limited. The milling chamber of the bead mill has an empty volume of 50 mL and it needed to be filled between approximately 65% (32.5 mL) and 85% (42.5 mL) with grinding beads. The size of the zirconium oxide beads used as grinding media was approximately 1 – 1.25 mm and the bead loading was maintained between 30 – 35 mL. It was estimated, in some trial experiments, that a minimum volume of approximately 75 mL was required to ensure proper recirculation of the dispersion in the mill. Based on the recommendations of the bead mill manufacturer and another study carried out by the authors, the duration of milling, the reliability and repeatability of the bead milling process was established [43].

It was considered to be important to ensure proper recirculation of the dispersions during bead milling. This was difficult to achieve in the case of high viscosity dispersions (as in the present case) because such dispersions were likely to ‘sit’ in the inlet funnel of the bead mill. To overcome this problem, an overhead stirrer was used in conjunction with the bead mill.

The overhead stirrer blade was placed in the inlet funnel of the bead mill and rotated at 400 – 500 RPM while milling a viscous dispersion. This facilitated the continuous flow of dispersion in the milling chamber through the feed zone.

4. Analytical techniques

4.1 Viscosity measurements

At numerous stages of the dispersion preparation and optimisation process, the viscosity profiles of a dispersion were recorded over a shear range of 1 s^{-1} to 1000 s^{-1}. For this purpose, a TA Instruments AR-1500 EX rheometer was employed. ASTM D4287-00(2010) standard method was used for measuring high shear viscosity (continuous ramp test) using a 60 mm stainless steel cone with 1° taper angle and 27 μm truncation gap.

4.2 Particle size analysis and zeta potential measurements

In the present study, a Zetasizer Nano ZS (Malvern Instruments) was used to analyse pigment particle size distribution in the waterborne dispersions that were prepared. For particle size analysis by DLS, the recommendation is to have a solids content of below 0.1% in the sample [44]. Thus, samples were prepared by diluting 0.25 g of pigment dispersion with 50 grams of deionised water and subjecting the diluted sample to ultra-sonication for five seconds. The default values of 1.675 for the refractive index and 1.00 for the absorption of the pigment were set in the instrument software. Due to the extent of dilution, water was selected as dispersant in the test SOP, for which the default values of 1.330 and 78.5 were used for refractive index and dielectric constant, respectively. The test sample was equilibrated at 25 °C for 60 seconds prior to recording the data. A disposable sizing cuvette (Malvern reference: DTS0012) was used for the size analyses. The test samples that were prepared for particle size analysis, were used for zeta potential measurements as well. A disposable zeta cell (Malvern reference: DTS1060C) was employed.

4.3 Ultra-centrifugation

Centrifugation is a widely used technique for characterising de-mixing phenomena such as sedimentation, flotation and/or consolidation. An analytical centrifuge is an instrument which evaluates the stability of a colloidal system by accelerated gravitational settling. A

LUMiSizer® dispersion analyser was used in this study to analyse the tendency to sedimentation of pigment in the optimised, waterborne pigment dispersions.

The working principle is such that the dispersion sample to be analysed is contained in a suitable cell (a LUM 2mm polycarbonate cell in this case) and secured horizontally in the instrument. Near infrared light (wavelength 870 nm) of known intensity (I_o) illuminates the entire sample as it is centrifuged. The intensity of transmitted light (I) through the sample is recorded by a detector consisting of 2048 CCD elements. The transmission profile recorded by the detectors is converted into space- and time-resolved extinction profiles over the entire sample length. The instrument is also capable of particle size analysis but in this study, it was employed only for accelerated gravitational sedimentation analysis replicating six months storage stability.

4.4 Electrical characterisation

The surface resistivity of drawdowns of dispersions was recorded using a Keithley digital multimeter (Model 2100). An electrode, designed to record the surface resistivity of a 30 mm x 30 mm printed area was used. A standard 5 kg weight block was used to press the electrode onto the printed substrate, thus helping to ensure that intimate contact between the electrode and the test surface was achieved.

5. Results and Discussion

5.1 Optimisation of pigment dispersions

The optimisation of the dispersions of each of the four pigments considered in this study was carried out following the procedure outlined in Section 3.1. As an example, the complete optimisation process for Carbon3, which is a very high surface area pigment, is presented and discussed in the following text. The data pertaining to the detailed optimisation and characterisation of the dispersions of Carbon1, Carbon2 and Carbon4 is provided as supplementary data for this study.

In order to select a dispersant for the study of the optimisation of the Carbon3 dispersion, a simple 'Sinking test' was performed by adding 0.08g of Carbon3 to the various dispersant solutions. As shown in Figure 1, the opacity of the Dispersant3 solution (760W) after 72 hours of pigment addition was significantly greater than that of the other dispersant solutions. Thus, Dispersant3 was used in attempts at optimising the binder-free dispersion of Carbon3.

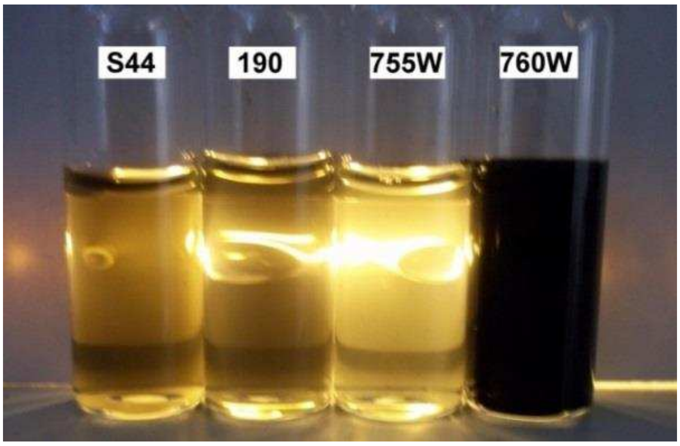


Figure 1: Dispersant solutions after 72 hours of addition of Carbon3

Using Equation 1, the theoretical required amount of dispersant for Carbon3 was calculated to be approximately 170% DOWP. A control dispersion containing 6 wt% (of the total formulation) of Carbon3 and 25 wt% (of the total formulation) of Glascol HN2 resin solids was prepared. In practice, the generally accepted viscosity of a control dispersion for equivalent systems is ≤ 1 Pa s at a shear rate of ≤ 50 s^{-1}. The Control dispersion of Carbon3, that was prepared as described above, met this criterion. Using the theoretical dispersant dosage, dispersions containing 8 wt% and 9.25 wt% Carbon3 were prepared and compared against the Control dispersion.

As shown in Figure 2, the viscosities of both of the dispersions containing 8 wt% Carbon3 and 9.25 wt% Carbon3, were lower than that of the control dispersion. However, the pigment loading could not be increased beyond 9.25 wt% due to the very high viscosity of the pre-mixed dispersion which made it difficult to re-circulate the dispersion in the bead mill properly. Thus, 9.25 wt% Carbon3 was considered to be the maximum achievable pigment loading when 170% DOWP of Dispersant3 was used.

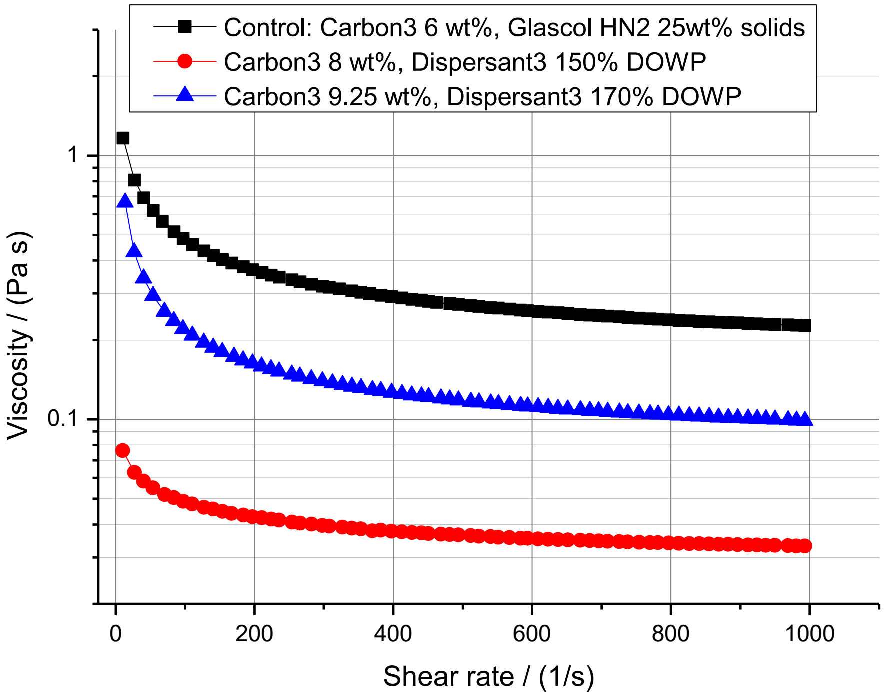


Figure 2: Viscosity profiles of dispersions of Carbon3 prepared in Step 2

In Step 3 of the dispersion optimisation process, a series of dispersions containing 9.25 wt% Carbon3 and various amounts of Dispersant3 (140%, 155%, 170% and 200% DOWP) was prepared. The least amount of Dispersant3 used was 140% DOWP because below this level the dispersant was likely to be well under-dosed, given the very high surface area of Carbon3. On the other hand, the maximum dispersant amount was 200% DOWP, chosen because upon further increasing the dispersant dosage, the pre-mixed dispersion possessed very high yield point which made it difficult to ensure effective recirculation in the bead mill.

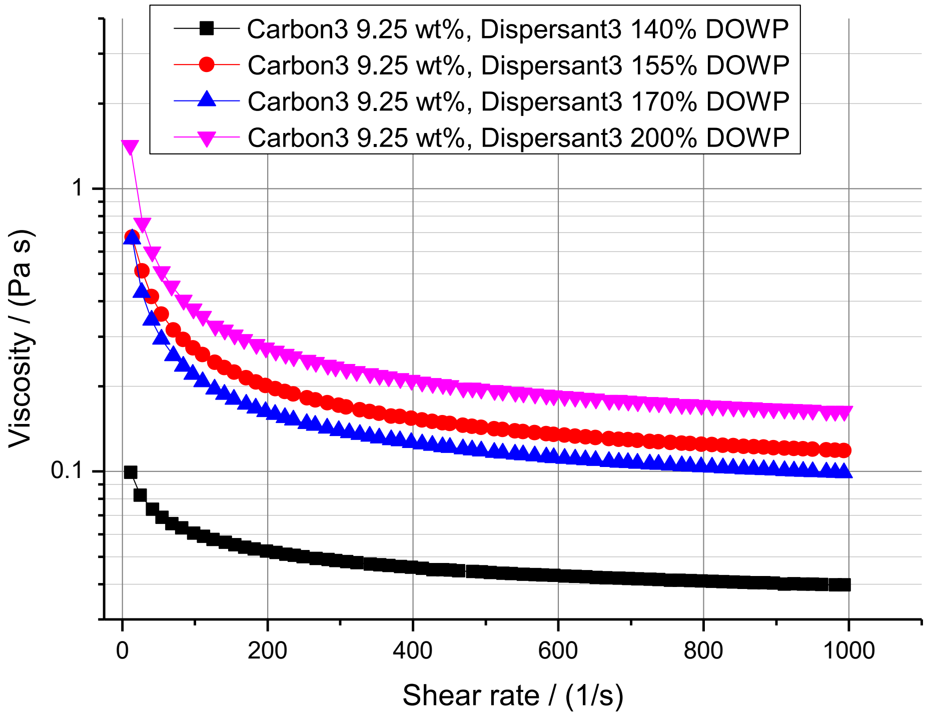


Figure 3: Viscosity profiles of dispersions of Carbon3, prepared in Step 3 of the optimisation process

Generally, an increase in the dispersion viscosity was observed upon increasing the dispersant dosage, as shown in Figure 3. The initial particle size analysis results indicated that the use of 200% DOWP of Dispersant3 resulted in the smallest average particle size, at 205.5 nm. The average particle size in the dispersion of Carbon3, prepared using 155% DOWP was very close to that in the dispersion prepared using 200% DOWP of Dispersant3. Furthermore, a uni-modal size distribution and a narrow PDI were observed for both of these dispersions. As shown in Table 4, the surface resistivity of the dispersion containing 155% DOWP was less than that of the dispersion containing 200% DOWP of Dispersant3. In order to establish with some confidence that the optimal dispersant dosage that was needed to stabilise the Carbon3 dispersion was around 155% DOWP, the dispersions were assessed for their storage stability.

Table 3: Results of zeta potential and particle size analysis of the dispersions of Carbon3 prepared using various dosages of Dispersant3

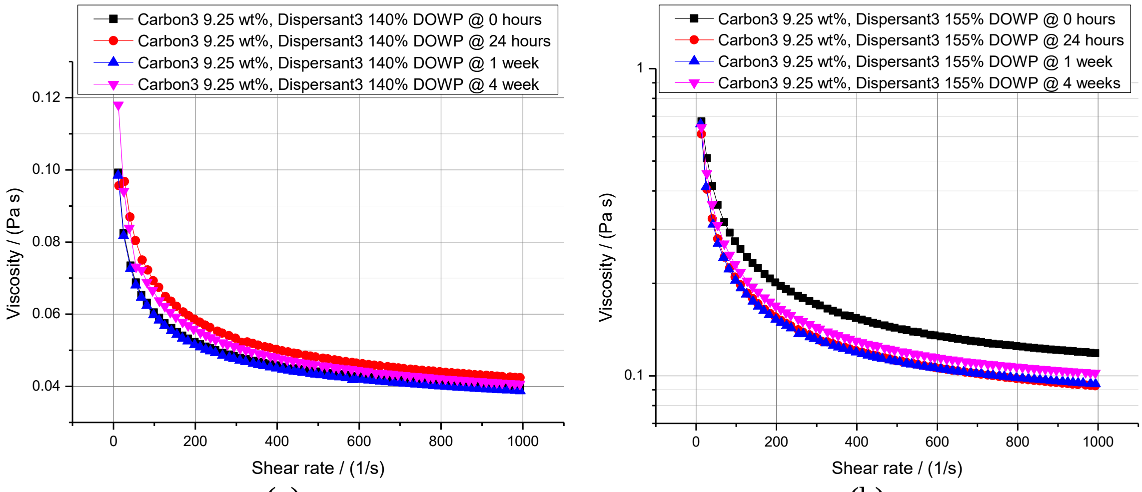
Dispersion composition	**ζ (mV)**	**Z-avg. (nm)**	**PDI**	**Peak 1 (nm)**	**Peak 2 (nm)**	**Peak 1 Area (%)**	**Peak 2 Area (%)**
Carbon3 9.25wt%, Dispersant3 140% DOWP	-25.8	271	0.332	338	5006	96.9	3.1

Carbon3 9.25wt%, Dispersant3 155% DOWP	-30.8	219	0.158	259	0	100	0
Carbon3 9.25wt%, Dispersant3 170% DOWP	-28.4	271	0.341	442	4571	98.3	1.7
Carbon3 9.25wt%, Dispersant3 200% DOWP	-6.23	205	0.180	259	0	100	0

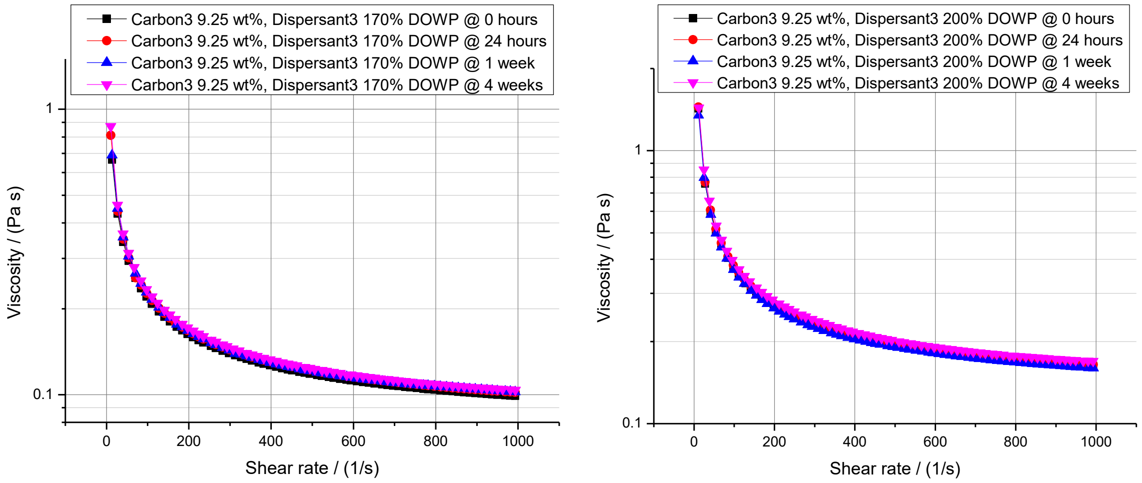
Table 4: Electrical characteristics of dispersions of Carbon3 prepared using various dosages of Dispersant3

Dispersion composition	**Conductivity (µS/cm)**	**Surface resistivity (Ω/☐)**
Carbon3 9.25 wt%, Dispersant3 140% DOWP	290	429
Carbon3 9.25 wt%, Dispersant3 155% DOWP	310	456
Carbon3 9.25 wt%, Dispersant3 170% DOWP	340	487
Carbon3 9.25 wt%, Dispersant3 200% DOWP	371	508

The viscosity profiles, presented in Figure 4, indicated that in all of the dispersions, shear thinning rheology was maintained upon storage, indicating that the state of dispersion of pigment probably did not change considerably. It was also noted that the viscosity of the dispersion containing 155 %DOWP decreased slightly during four weeks of storage.



(a) (b)



(b) (c)

Figure 4: Viscosity stability analysis of the dispersions containing 9.25 wt% Carbon3 and (a) 140%, (b) 155%, (c) 170% and (d) 200% DOWP of Dispersant3.

The results of particle size analyses carried out on samples that had been stored are presented in Table 5. The average particle size as well as PDI of the dispersion containing 140% DOWP of Dispersant3 decreased considerably and unlike the other dispersions in the series, the particle size distribution remained consistently uni-modal. In the dispersions containing greater dispersant dosages, the average particle size decreased or fluctuated within a reasonably broad range. However, a second peak, well above 4000 nm, was regularly observed in the particle size distribution. It was also noticed that in comparison to the dispersions containing 170% and 200% DOWP, the area of Peak 2 was generally smaller in the particle size distribution of the dispersion prepared using 155% DOWP of Dispersant3.

Table 5: Results of particle size analyses of the dispersions containing 9.25 wt% Carbon3 and various amounts of Dispersant3

Dispersion composition	**Time**	**Z-avg. (nm)**	**PDI**	**Peak 1 (nm)**	**Peak 2 (nm)**	**Peak 1 Area (%)**	**Peak 2 Area (%)**
Carbon3 9.25wt%, Dispersant3 140% DOWP	0 hours	271	0.33	338	5006	96.9	3.1
	24 hours	221	0.17	252	0	100	0
	1 week	226	0.21	336	0	100	0
	4 weeks	202	0.13	237	0	100	0
Carbon3 9.25wt% Dispersant3 155% DOWP	0 hours	219	0.16	259	0	100	0
	24 hours	314	0.36	466	4978	98.7	1.3
	1 week	226	0.22	269	4566	97.2	2.8
	4 weeks	226	0.15	253	0	100	0
Carbon3 9.25wt%,	0 hours	271	0.34	442	4571	98.3	1.7

Dispersant3 170% DOWP	24 hours	222	0.22	250	4569	96.7	3.3
	1 week	214	0.17	228	5047	98.4	1.6
	4 weeks	201	0.20	218	4192	95.6	4.4
Carbon3 9.25wt%, Dispersant3 200% DOWP	0 hours	205	0.18	259	0	100	0
	24 hours	244	0.26	333	4778	97.6	2.4
	1 week	226	0.22	248	4632	96.3	3.7
	4 weeks	224	0.26	292	4857	98.4	1.6

On the basis of the results of the rheological characterisations, particle size analyses and electrical characterisations, it was concluded that a dispersant dosage of greater than 155 %DOWP did not result in an improved dispersion of Carbon3. The dispersions that were prepared using 140% and 155% DOWP of Dispersant3 possessed fairly similar characteristics. Considering the fact that a slight increase was recorded in the viscosity of the dispersion that was prepared using 140% DOWP of Dispersant3, a greater dispersant dosage, i.e. 155% DOWP, was used to prepare the optimised dispersions of the pigment, in the next step.

During the preparation of the pre-mixed dispersions, in Step 4 of the optimisation process, it was found that the maximum amount of Carbon3 pigment that could be dispersed using 155% DOWP of Dispersant3, while keeping the viscosity low enough for bead milling, was 11 wt% of the total formulation. Thus, pre-mixed dispersions containing 11 wt% of the Carbon3 pigment were prepared using 155% DOWP of Dispersant1 and Dispersant2, respectively. The viscosity profiles of the bead milled dispersions are presented in Figure 5 which clearly indicates that Dispersant3 limited the maximum amount of Carbon3 pigment that could be added in the dispersion under the prevailing conditions.

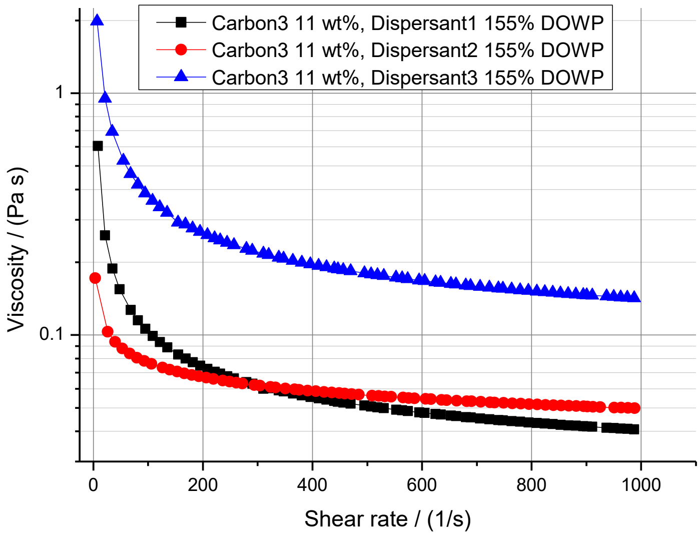
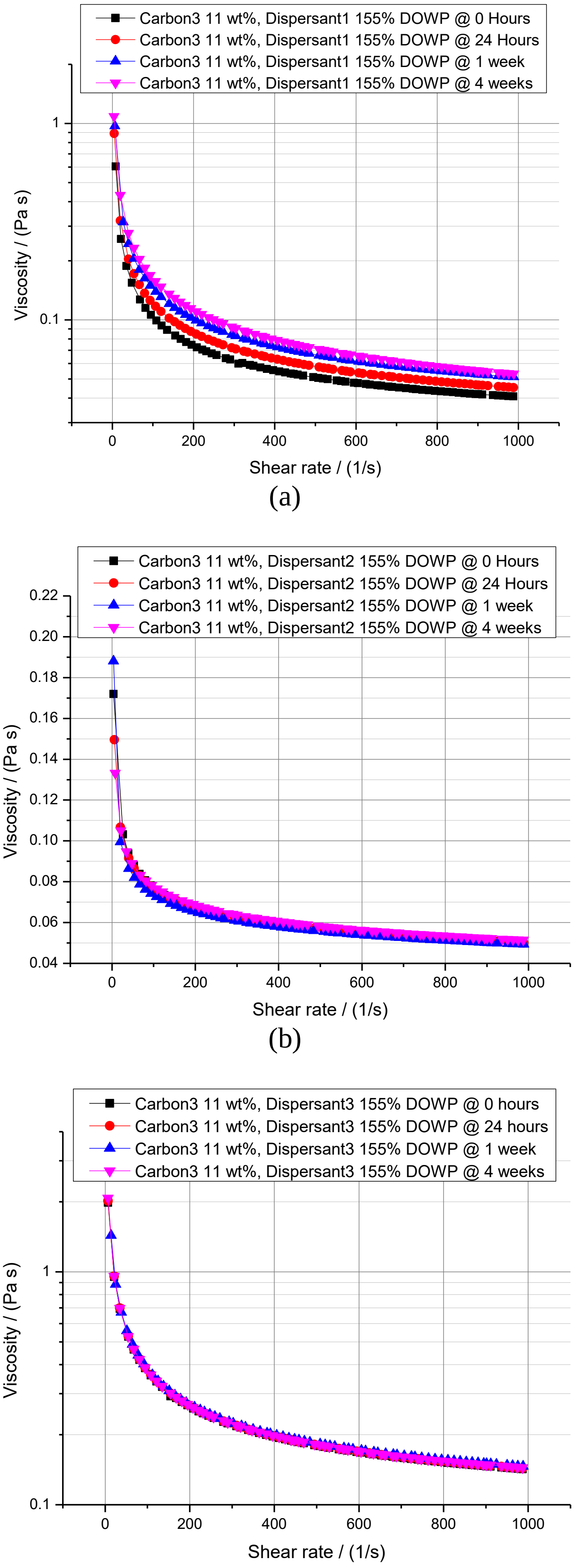


Figure 5: Viscosity profiles of dispersions of Carbon3 prepared in Step 4

As in case of dispersions of other pigments, the stability of the Carbon3 pigment dispersions was analysed by recording the viscosity profiles during four weeks of storage. As shown in Figure 6(a-c), all of the dispersions possessed very stable, shear thinning viscosity profiles. However, the average increase in viscosity was more pronounced in the case of Carbon3-Dispersant1 dispersion. The relevant data is provided in Table 6.

The results of particle size analyses carried out on Carbon3 pigment dispersions, prepared using optimum %DOWP of various dispersants, are presented in Table 7. It was observed that the extent of aggregation was more pronounced in the dispersion of Carbon3 prepared using Dispersant1. In contrast, the dispersions that were prepared using Dispersant2 or Dispersant3 possessed fairly stable particle size distribution during storage. These results correlate strongly with the results of viscosity stability analysis carried out on the different dispersions of Carbon3.



(a)

(b)

(c)

Figure 6: Viscosity stability of the dispersions of Carbon3 prepared using 155 %DOWP of (a) Dispersant1, (b) Dispersant2 and (c) Dispersant3

Table 6: Average increase in viscosity of Carbon3 dispersions prepared in Step 3

Dispersion name	**Average increase in viscosity (%)**	**St. Dev.**
Carbon3-Dispersant1	41.92	8.89
Carbon3-Dispersant2	2.79	0.87
Carbon3-Dispersant3	1.05	0.29

Table 7: Results of particle size analyses carried out on the optimised dispersions of Carbon3

Dispersion composition	**Time**	**Z-avg (nm)**	**PDI**	**Peak 1 (nm)**	**Peak 2 (nm)**	**Peak 1 Area (%)**	**Peak 2 Area (%)**
Carbon3 11wt%, Dispersant1 155% DOWP	0 hours	203	0.28	243	2161	89.9	10.1
	24 hours	206	0.24	250	3650	95.7	4.3
	48 hours	215	0.24	250	4043	95.1	4.9
	1 week	300	0.28	422	4791	98.7	1.3
	4 weeks	210	0.20	247	4946	98.6	1.4
Carbon3 11wt%, Dispersant2 155% DOWP	0 hours	195	0.14	228	0	100	0
	24 hours	189	0.22	207	4672	96.5	3.5
	48 hours	250	0.28	384	0	100	0
	1 week	224	0.24	287	4593	98.2	1.8
	4 weeks	201	0.16	242	4592	98.4	1.6
Carbon3 11wt%, Dispersant3 155% DOWP	0 hours	202	0.22	248	4823	98.3	1.7
	24 hours	229	0.26	342	0	100	0
	48 hours	193	0.15	230	0	100	0
	1 week	204	0.19	258	0	100	0
	4 weeks	221	0.25	303	4385	98.7	1.3

The results of various analyses presented above, indicate that the optimised dispersion of Carbon3, which was prepared using Dispersant2 or Dispersant3, was very stable. In contrast, a considerable increase in the viscosity of the Carbon3-Dispersant1 dispersion was recorded. However, an instant shear thinning rheology was maintained. Furthermore, the surface resistivity of the drawdown of this dispersion was similar to that of the other dispersions of Carbon3 (The results of electrical characterisation are provided in Table 8). Consequently, it was decided to use all of the three optimised dispersions of Carbon3 in the let-down studies.

Table 8: Electrical characteristics of the optimised dispersions of Carbon3

Dispersion composition	Surface resistivity (Ω/□)
Carbon3 11 wt%, Dispersant1 155% DOWP	395
Carbon3 11 wt%, Dispersant2 155% DOWP	387
Carbon3 11 wt%, Dispersant3 155% DOWP	391

5.2 Comparison of Low surface area and High surface area pigments

The complete optimisation process, as discussed in the preceding section, yielded the formulations tabulated in Table 9. It is evident, as expected, that the maximum amount of high surface pigments that could be added in the formulations was considerably lower compared to the amounts of low surface area pigments. On the other hand, the dispersant dosage was unusually higher for the high surface area pigments.

Table 9: Maximum pigment loading and optimised dispersant dosage

S. No	Pigment		Dispersant	
	Name	Max. Quantity (wt%)	Name	Optimised % DOWP
1	Carbon1	31	Dispersant3	15
2	Carbon2	23	Dispersant1	17.5
3	Carbon3	11	Dispersant3	155
4	Carbon4	9.25	Dispersant1	225

One of the main objectives of the present study was to investigate the applicability of the 'ladder experiments' approach in preparation of stable dispersions of electrically conductive and high surface area carbon black pigments. More specifically, the aim was to establish if the typical optimization process could be used to prepare stable dispersions of non-printing ink grades of carbon black pigment. This was done on the basis of results of rheological characterization, accelerated gravitational settling and assessment of electrical properties, as discussed in the following sections.

5.2.1 Rheological characterization during storage

The pigment dispersions formulated by following the complete optimization process were tested for stability of their rheology. For this purpose, the viscosity profiles were recorded during four weeks of storage. As shown in Figure 7(a-b), the dispersions of low surface area pigments possessed very stable, shear thinning viscosity profiles with little or no increase in the viscosity over the tested shear rate range. In the case of dispersions of high surface area pigments, Carbon3 dispersion possessed remarkably stable viscosity and there was virtually no change during four weeks of storage as shown in Figure 7(c). However, for the dispersion of Carbon 4, a gradual increase in the viscosity was observed, but shear thinning profile was maintained during storage. This is shown in Figure 7(d).

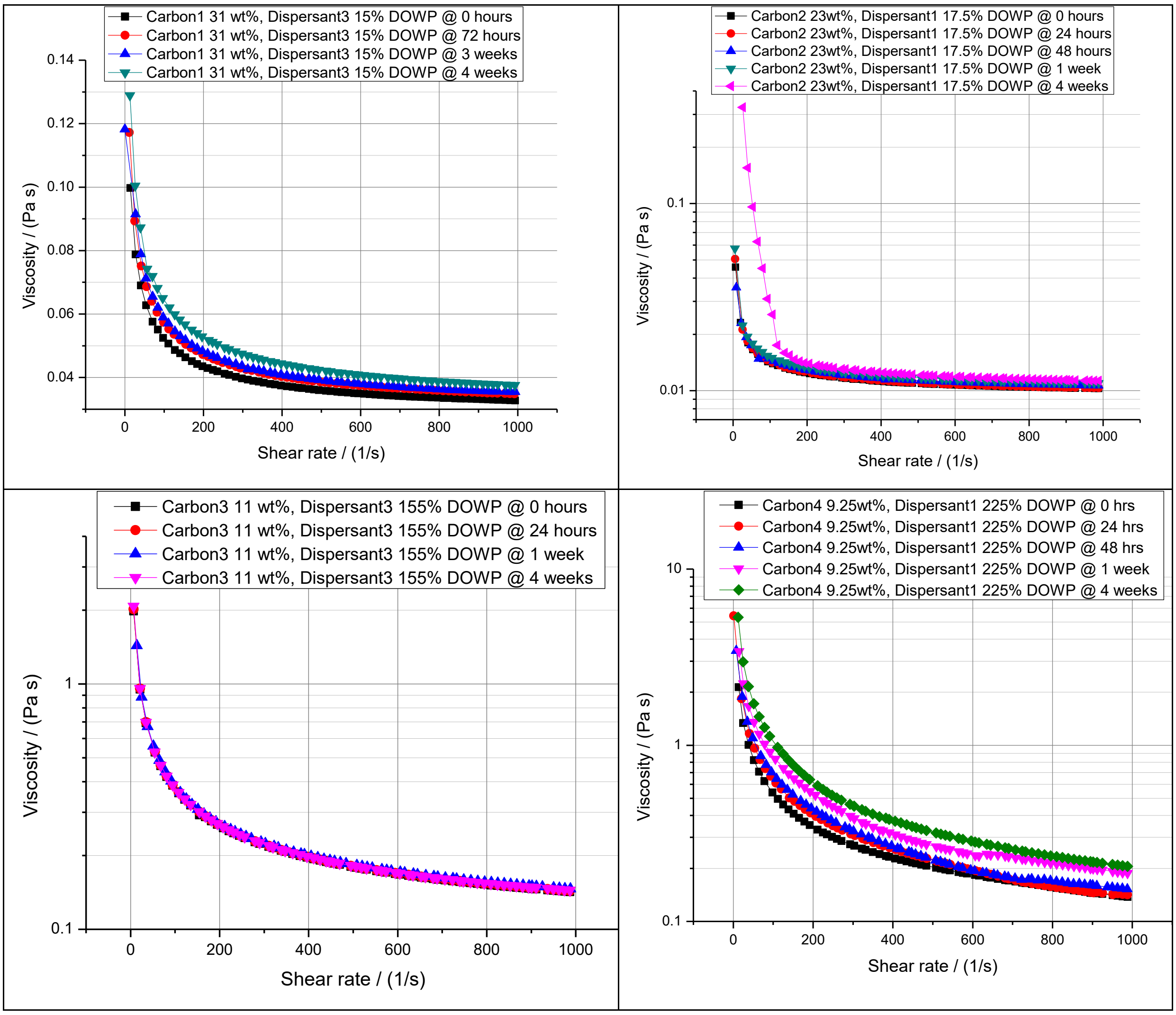


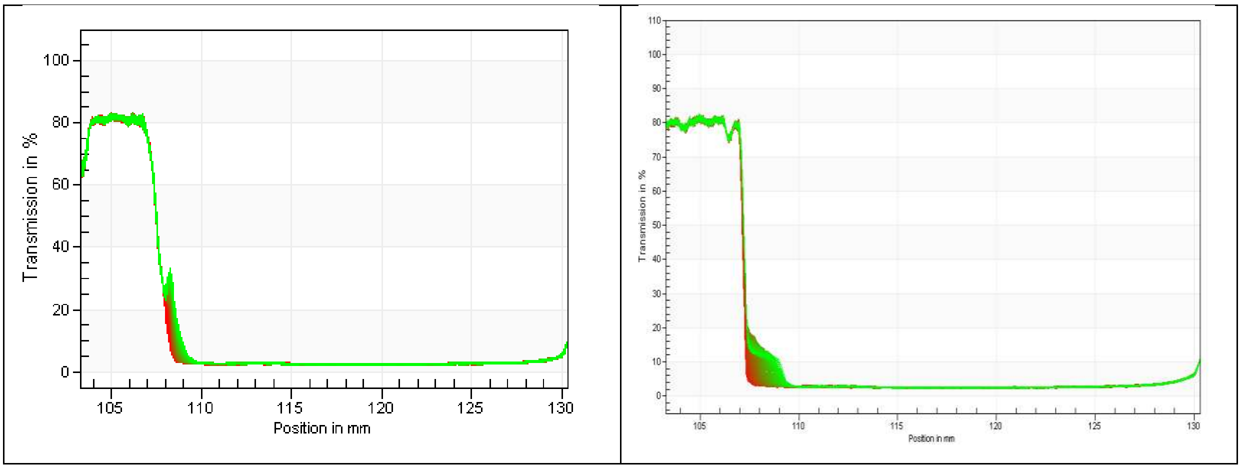
Figure 7: Rheological profiles recorded over four weeks of storage. (a) Carbon1-Dispersant3, (b) Carbon2-Dispersant1, (c) Carbon1-Dispersant3 and (d) Carbon4-Dispersant1

5.2.2 Accelerated gravitational settling

In this study, rheological characterisation, particle size analysis and zeta potential measurements provided insight into the stability of the pigment dispersions. The results of these analyses were generally found to complement each other and provided a rather clear indication that the dispersions prepared using the optimum %DOWP of various dispersants were stable for up to four weeks after preparation. Among the few techniques that can be employed to characterise a dispersion without diluting it, centrifugation (or ultra centrifugation) is the more commonly used. The primary advantage is that the dispersion properties are not modified during sample preparation [45]. In this respect, analytical centrifugation has significant potential and it is increasingly being used in the industry.

The data obtained from modern analytical centrifuges can be processed to characterise dispersion properties, such as particle size distribution, quantitatively. However in this study, the transmission profiles obtained during centrifugation of a dispersion were analysed to obtain qualitative description of the extent of sedimentation of pigment in the dispersion. To replicate six months storage, the transmission profiles of the undiluted dispersion samples were recorded following the procedure outlined in Section 4.3. In the sets of transmission lines presented in Figure 8, the red lines show the transmission profiles recorded at the start of centrifugation while the green lines represent the transmission profiles recorded towards the end of test.

During centrifugation of the dispersion of Carbon1 pigment prepared using Dispersant3, the maximum light transmission through the upper 1 mm (approx.) of the dispersion was 30% (approx.). The first recorded transmission profile of Carbon2-Dispersant1 is characterised by virtually no transmission while the transmission profiles recorded towards the end of the test show that the transmission through the upper 2 mm (approx.) of the dispersion was between 18% and 10% (approx.). There was no recordable increase in the light transmission through the Carbon3 and Carbon4 pigment dispersions which were tested.



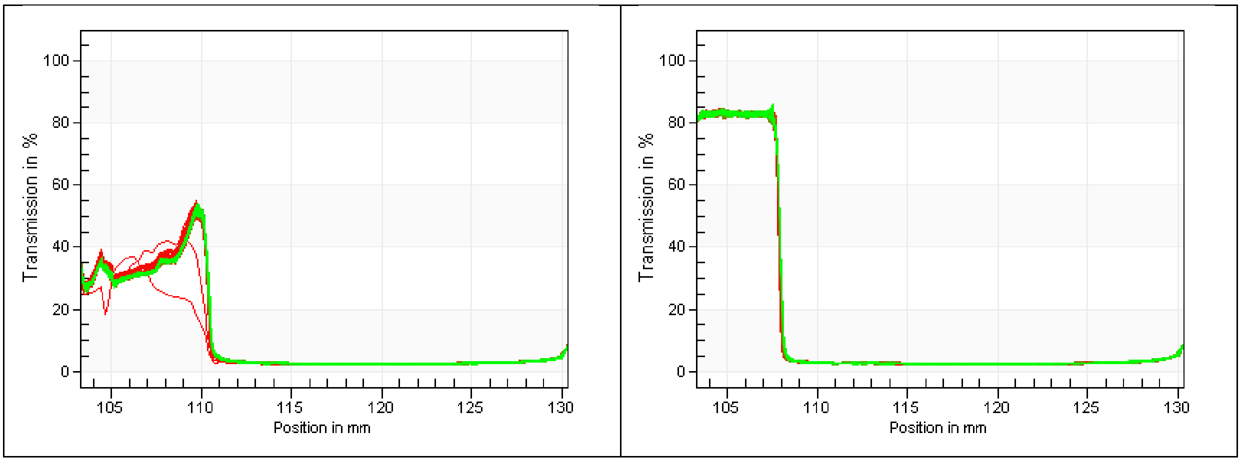


Figure 8: Transmission profiles recorded during ultra-centrifugation of (a) Carbon1-Dispersant3, (b) Carbon2-Dispersant1 (c) Carbon3-Dispersant3 and (d) Carbon4-Dispersant1

In this study, the analytical centrifugation tests were not carried out to characterise the sedimentation of dispersed pigment quantitatively. However, the test results presented above clearly indicate that the optimised dispersions of Carbon1, Carbon2, Carbon3 and Carbon4 were very stable in terms of settling/sedimentation of the pigment particles during at least six months of storage.

5.2.3 Electrical properties of the optimised dispersions

The electrical characteristics of the optimized dispersions were studied by measuring the surface resistivity of the drawdowns of these dispersions. The drawdown method was selected due to the fact that the film deposit achieved through this method resembles the ink layer deposits produced in printing. It is worth mentioning at this stage that from this point onwards in this paper and in the Part B of this paper, the results of all the tests carried out on all twelve optimized dispersions are presented. This allows to clearly depict in what respects the various dispersions were different from one another.

From the results presented in Table 10, it is clear that the dispersions of a pigment prepared using different dispersants generally possessed comparable surface resistivities. The other, and arguably the most striking feature is that, despite the significantly lower pigment loadings, the surface resistivities of the dispersions of high surface area pigments were also comparable to a considerable extent with those of the low surface area pigment dispersions, particularly in the case of Carbon3.

Table 10: Surface resistivity values of drawdowns of dispersions optimised and characterised in the present study

Dispersion composition	**Surface resistivity (Ω/☐)**
Carbon1 31 wt%, Dispersant1 15% DOWP	321
Carbon1 31 wt%, Dispersant2 15% DOWP	332
Carbon1 31 wt%, Dispersant3 15% DOWP	265
Carbon2 23 wt%, Dispersant1 17.5% DOWP	241
Carbon2 23 wt%, Dispersant2 17.5% DOWP	234
Carbon2 23 wt%, Dispersant3 17.5% DOWP	225
Carbon3 11 wt%, Dispersant1 155% DOWP	390
Carbon3 11 wt%, Dispersant2 155% DOWP	378
Carbon3 11 wt%, Dispersant3 155% DOWP	371
Carbon4 9.25 wt%, Dispersant1 225% DOWP	575
Carbon4 9.5 wt%, Dispersant2 225% DOWP	390
Carbon4 9 wt%, Dispersant3 225% DOWP	456

6. Conclusions

In this study, electrically conductive grades of carbon black pigment were used to prepare and optimize waterborne, binder-free dispersions. Our results show that the typical binder-free dispersion preparation process can be employed to prepare dispersions of non-printing ink grades of carbon black pigments. Most importantly, the rheological characterization, particle size analyses, sedimentation studies and electrical properties clearly show that the devised process yields stable dispersions of even the very high surface area pigments. It is also noteworthy that very high surface area carbon black pigments, which are generally not considered for printing ink formulation, can be used in considerably lower amounts to achieve high electrical conductivity in waterborne dispersions.

Theoretically, if the high surface area carbon blacks were dispersed down to their primary particle size, they would have particle sizes < 20 nm. This can only be done using specialist “nano" mills which can accommodate very low grinding media, usually Zirconia bead size of ≤ 0.3 mm. In practice the average ink manufacturer will have milling equipment available that is equivalent to the type used in this study. Thus, certainly the choice of the mill and the process used is much more relevant to the industry. Furthermore, there is often a concern when dispersing high surface area carbon blacks for conductive coatings, about the potential for polymeric dispersants to form an "insulating layer" around the carbon particles and so negatively affecting the current flow. However, our study does not seem to verify this.

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Data availability

The raw/processed data required to reproduce these findings cannot be shared at this time as the data also forms part of an ongoing study.

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