JOURNAL OF MATERIALS SCIENCE **36** (2001) 4419–4431

Factors affecting the adsorption of stabilisers on to carbon black (flow micro-calorimetry studies)

Part II *Hindered amine light stabilisers (HALS)*

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The interaction of hindered piperidine light stabilisers (HALS) with carbon black has been examined using flow micro-calorimetry (FMC) and Fourier transform infrared spectroscopy (FTIR). Significant differences in both the overall adsorption activity and molar heats of probe adsorption are observed. Differences in adsorption behaviour between different types of carbon black were clearly evident and, as with a previous paper (see reference 1, in the latter paper, surface chemistry of the carbon blacks investigated is extensively analysed by XPS, FTIR, N_2 BET adsorption and Karl–Fischer analysis), were mainly to be due to differences in carbon black surface chemistry. The specific surface area merely physically affected the level and heat of adsorption (per unit mass of carbon black). Variation in the degree of substitution of the piperidine amine is an important factor that is found to influence the adsorption activity of HALS, as well as the number of adsorption active and sterically accessible functional groups per HALS molecule. In some cases the adsorbed HALS could be detected by FTIR; shifts in absorption frequencies associated with both the adsorbate and the substrate yielded significant insight into the mode of adsorption of several of the HALS investigated.

1. Introduction

In the first part of this series of papers [1], factors affecting the adsorption of primary phenolic antioxidants on to carbon black were investigated. Prior to this investigation, the surface characteristics of the carbon blacks were extensively characterised by XPS, FTIR, N_2 BET adsorption studies and Karl–Fisher analysis. The surface chemistry of the carbon black was found to play a significant role in the adsorption activity. Increasing the concentration of oxygen containing functional groups up to a certain critical value generally increased adsorption activity. However, once this value had been exceeded (as in the case of a highly oxidised carbon black) adsorption activity reduced. This was thought to be due to mutual interaction between adjacent functional groups and due to the strongly adsorbed water molecules grouped around active sites, the so called "hydrogel effect". Steric hinderance of the phenolic OH by alkyl groups was found to significantly effect adsorption activity. Carbonyl groups in antioxidant molecules were also show to contribute to adsorption activity.

Hindered amine light stabilisers (HALS) are an important class of protective agents which almost universally form a part of stabiliser packages. It is also therefore necessary to study the adsorption of HALS on to the same series of carbon blacks as investigated in the previous paper [1]. HALS feature some interesting adsorption active functionalites such as amines (e.g., hindered piperidines) and triazines. In this study the adsorption of a range of HALS will be investigated using FMC and insight into the mode of adsorption will be acquired via FTIR studies on carbon black samples recovered from the FMC cell after the adsorption experiment. Precise molecular structural factors affecting adsorption such as the degree of substitution of piperidine will be investigated using a series of model compounds.

2. Experimental procedures

2.1. Materials

The HALS investigated are detailed in Table I and were Chimassorb 944®, Chimassorb 119®, Tinuvin 770®, Tinuvin 622 LD®, Uvasil 299/299 LM® and ADKASTAB LA 82. The amino model compounds used in order to study the steric hindrance of piperidine group were: Piperidine, 2,6-*cis*-Dimethylpiperidine (DMPP), 2,2′,6,6′-Tetramethyl-piperidine

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TABLE I Commercial HALS investigated

Trade name (supplier)	Systematic name	Molar mass
Chimassorb 944® (Ciba)	Poly {6-[(1,1,3,3,-tetramethylbutyl)-imino]-1,3,5-triazine-2,4-diyl]-[2,2,6,6,-tetramethypiperidyl)-imino]-hexamethylene-[4-2,2,6,6,-tetramethypiperidinyl)-imino}	$\sim$ 3000–$>$ 2500
Chimassorb 119® (Ciba)	1,3,5-triazine-2,4,6-triamine,N,N'-1,2-ethane-diyl-bis[[[4,6-bis-[butyl-1,2,2,6,6,-pentamethyl-4-piperidinyl)amino]-1,3,5-triazine-2-yl]imino]-3,1-propanediyl]] bis [N,N″-dibutyl N,N″bis-(1,2,2,6,6,-pentamethyl-4-piperidinyl)-	2286
Tinuvin 770® (Ciba)	Bis(2,2,6,6,-tetramethyl-4-Piperidyl) sebacate	481–480.74
Tinuvin 622 LD® (Ciba)	butanedioic acid, polymer with 4-hydroxy-2,2,6,6-tetramethyl-1-piperidineethanol	>2500
Uvasil 299/299 LM® (Enichem)	Polymethylpropyl 3-oxy-[4(2,2,6,6,-tetramethyl) piperidinyl] siloxane	1100–2500
ADEKASTAB LA 82® (Adeka)	(2,2,6,6,-tetramethyl-4-(1-methylpiperidyl)) acrylate	239

TABLE II Properties of carbon blacks studied

	Surface area (m^2 g^{-1})		Particle size[b]	Iodine number	DBPA pellets	Volatile content[b]		Water content[c]
CB type	STSA[a]	N_2 BET	(nm.)	(mg g^{-1})	cm^3/100g	(%)	pH[b]	% wt. CB
CB-A	86.8	107.1	22	119.6	96.6	1.5	8.5	1.01
CB-B	79.3	81.1	25	79.2	101.6	1	8.5	1.08
CB-C	85.1	113.2	25	78.2	72.5	3.5 ± 1	2.5	2.56
CB-D	370.5	542.8	13	173.3	91.3	8.5-12	2.5	8.59

[a] Standard thickness surface area.
[b] Obtained from Cabot North American Technical report) [3].
[c] Obtained by Karl–Fisher measurements.

(TMPP), 1,2,2′,6,6′-Pentamethyl-piperidine (PMPP) and 4-Amino 2,2′,6,6′-tetramethyl-piperidine (ATMP), (all from Aldrich). The structures of the HALS and piperidine model compounds are shown in Figs 1 and 2, respectively. The solvents n-heptane, cyclohexane and chloroform were of HPLC grade (Aldrich) and were stored over freshly activated (350°C/6 hours) 4A molecular sieves.

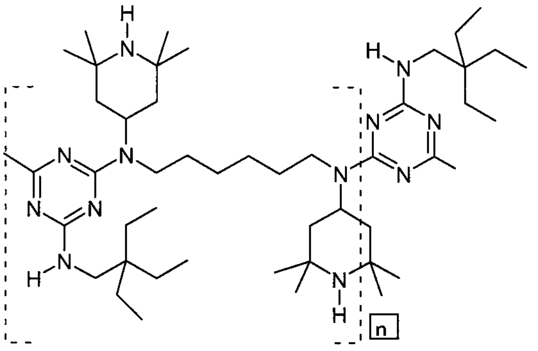
The four carbon blacks investigated were supplied by the Cabot Corporation and are the same as used in the first paper in this series [1]. Their main characteristics are given in Table II. These samples are not treated with any form of binder, therefore the data obtained should reflect their true surface chemistry, including of course any atmospheric effects such as adsorption of water. In the first paper the carbon blacks were subjected to rigorous surface chemical analysis involving XPS and FTIR. Tables III and IV summarise these findings in terms of the elemental distribution and the detailed functional group distributions, respectively.

TABLE III Surface elemental compositions of the different carbon blacks

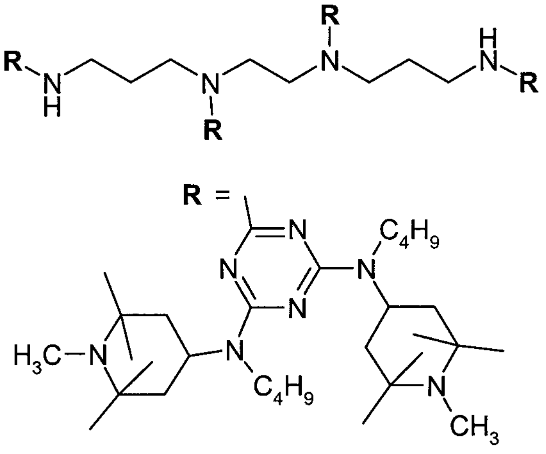
CB sample	% C	% O	% S	% N	O/C	S/C	N/C
CB-A	99.44	0.55	0.02	0	0.0055	0.0002	0
CB-B	98.48	0.96	0.54	0	0.0097	0.0055	0
CB-C	95.54	3.73	0.34	0.39	0.0390	0.0036	0.0041
CB-D	93.8	5.77	0.23	0.18	0.0615	0.0025	0.0019

TABLE IV Detailed functional composition (ratio O/C, S/C) of the different carbon blacks

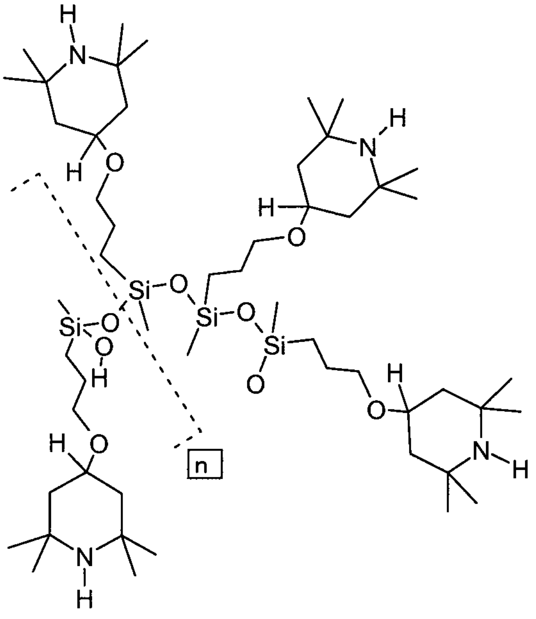
Sample	O=C O-S Carboxylic Aldehyde, Ketone,	O-C Hydroxyl, Ethers	O-C Phenol Anhydride	H_2O O_2	S-C	SO_2 Sulphones	SO_4 Sulphates	C-N	NO_2
Binding energy	531.5 eV	533.1 eV	534.5 eV	535.8 eV	163.8 eV	166.4 eV	168.8 eV	400 eV	405 eV
CB-A	0	0.0049	0	0.0006	0.0002	0	0	0	0
CB-B	0	0.0082	0	0.0006	0.0043	0.0006	0.0003	0	0
CB-C	0.0163	0.0127	0.0046	0.0024	0.0023	0.0005	0.0006	0.0027	0.0014
CB-D	0.0245	0.0238	0.0068	0.0037	0.0008	0	0.0016	0.0019	0



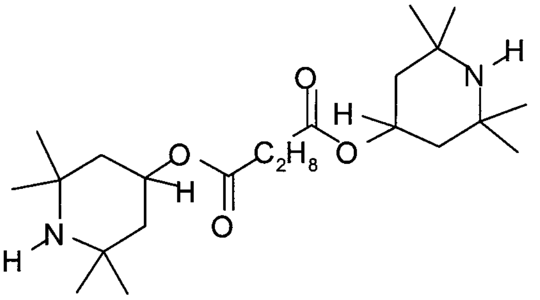
(a) Chimassorb 944®.



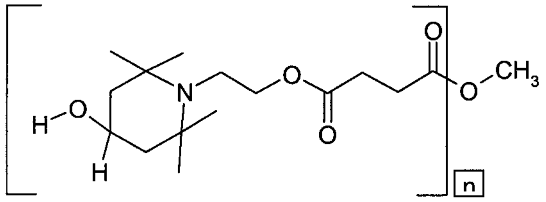
(b) Chimassorb 119®.



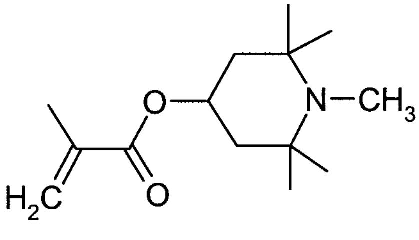
(c) Uvasil 299 LM®.



(d) Tinuvin 770®.



(e) Tinuvin 622 LD®.



(f) ADEKSTAB LA 82

Figure 1 Structures of hindered amine light stabilisers investigated.

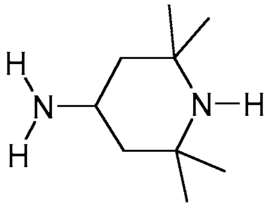
2.2. Surface characterisation of carbon blacks

The XPS spectra carbon blacks were obtained with a SSI-X probe (SS-100/206) spectrometer from Fisons (Surface Science Laboratories, Mountain View, CA), equipped with an aluminium anode (10 kV, 17 mA) and a quartz monochromator. The binding energies of the peaks were determined by setting the C (1s) component due to carbon only bound to carbon and hydrogen at a value of 284.2 eV. The peaks were curve fitted using a non-linear least squares routine and assuming a Gaussian/Lorentzian (85/15) function. Further details can be found in part I [1].

Transmission FTIR was carried out on the unmodified carbon blacks and on air dried samples recovered from the FMC cell, after completion of the adsorption–desorption experiments. The samples were diluted to 0.09% carbon black with dried KBr (3 hours at 300°C),

(a) piperidine (b) 2,6 *cis*-Dimethyl-piperidine.

(c) 2, 2', 6, 6'-Tetramethyl-piperidine (d) 1, 2, 2', 6, 6'-Pentamethyl-piperidine



(e) 4-amino 2, 2', 6, 6'-tetramethyl-piperidine

Figure 2 Structures of piperidine model compounds with increasin steric hinderance.

and a 0.2 g disc then pressed in the usual manner. The discs were placed in a transmission cell fitted to a Nicolet 510 FTIR spectrophotometer (DTGS detector) with dry-CO_2 free air purging. Spectra were made up of 500 scans with a resolution of 2 cm^{-1}.

In order to determine the water content of the pure carbon blacks studied, Karl Fisher tests were performed with a Kyoto MKC210 titrator coupled to an ADP-351 evaporator at 200°C in 20 min.

2.3. FMC studies

The FMC used was a Microscal 3V that has been upgraded to the all PTFE fluid path "I" (inert) specification. The Instrument was linked to the Microscal thermistor Bridge-control unit whose output was fed to a Perkin-Elmer 900 series interface. The cell outlet was connected to a Waters 410 differential refractometer whose data was fed into the second channel of the 900 series interface. Other details are described in Part I.

For most of the additives, the carrier fluid was *n*-Heptane (Aldrich HPLC grade) stored over freshly activated (350°C, 3 hours) 4A molecular sieve. Chloroform was used with additives that did not dissolve in *n*-Heptane, i.e., Irganox 245® because of its polar nature. Decahydronaphthalene was used as the non-adsorbing probe.

The basic FMC experimental conditions were conducted using a cell temperature of 27°C (±1°C) and a probe concentration of 0.03% w/v. The solvent flow rate was 3.30 cm^3 hr^{-1}. Sample size was 67.5 mg (±0.5 mg). The differential refractometer conditions were performed with a cell temperature of 40°C and sensitivities of 4. Samples were left to equilibrate at a carrier fluid flow rate of 0.033 cm^3 hr^{-1} over night. The flow rate was then increased to 3.3 cm^3 h^{-1} and the system left to settle for ca. 1 hr. Data collection was started and after 5–10 minutes the inlet was switched from carrier fluid to the solution of the probe in the carrier fluid. After the RI data reached a stable limiting value (typically 80 to 110 minutes) the inlet was switched back to carrier fluid and the desorption processes recorded and the run terminated. Thermal calibration was carried out with 2–3 peaks being generated. The differential refractometer is then calibrated using the 20 μl loop, 7–8 calibration peaks were obtained. Non-adsorbing probe data was obtained once for each carbon type. Please refer to Part I or other publications [2] for details of data analysis.

3. Results and discussion

3.1. Characterisation of the carbon blacks

The characterisation of the carbon black surface chemistry was carried out using X-ray photoelectron spectroscopy (XPS), FTIR, BET, Iodine adsorption and Karl–Fisher measurements. Additional data were obtained from a Cabot North American Technical report [3] . The findings of these analyses are described in detail in Part I [1] therefore only essential details will be given here.

The water content, volatile content and pH can be related to the hydrophilic character of the carbon black particle. For example, CB-D and CB-C have been oxidised with nitric acid and therefore have a higher surface concentration of oxygen containing functional groups than CB-B and CB-A. The FTIR and XPS analysis effectively confirms the latter. The differences between the STSA specific surface area and the N_2 BET specific surface area can be related to the porosity of the carbon blacks. Data shown in Table II, together with literature data [4, 5], indicates that CB-D is likely to have a porous surface. Micro-pores (<2 nm), meso-pores and macro-pores are present in this sample and are likely to affect its adsorption behaviour.

3.1.1. FTIR and XPS studies on unmodified carbon black

The major findings will only be summarised here as a more detailed interpretation is given in Part I [1]. It is immediately evident that only the oxidised samples CB-C and CB-D show obvious evidence of carbonyl species, with CB-D showing the slightly stronger absorption [1]. CB-A and CB-B do not show any IR spectral evidence of carbonyl species. All samples show a broad O-H stretching band, which can be assigned to adsorbed water. It is also important to note that a broad band centred at 1600 cm^{-1} was present on all the samples. This is mainly associated with the polyaromatic structure of the carbon black, however, it has been shown to hide some carbonyl and phenolic species which are detectable by XPS (Table IV).

The XPS data generally confirms the IR data but provides far more detailed information on the surface chemistry. The oxygen content can be ranked as follows and is in the ratio 1.00:1.75:6.78:10.49 (Table III).

$$\text{CB-A} < \text{CB-B} < \text{CB-C} < \text{CB-D}$$

Only CB-C and CB-D show evidence of carbonyl species (in the ratio of 1.00:1.50), such as carboxylic acids, aldehydes and ketones (Table IV). Such species reflect the strongly oxidising treatments to which these samples have been subjected. CB-A and CB-B show evidence of hydroxyl and ether oxygen in the ratio of 1.00:1.67. If CB-C and CB-D were included in this ranking, their respective ratios will be 2.59:4.86. CB-B has the highest level of sulphur (0.54% w/w), mainly in the form of S-C species (Table IV), reflecting the relative impurity of the oil feed stock used to produce this sample.

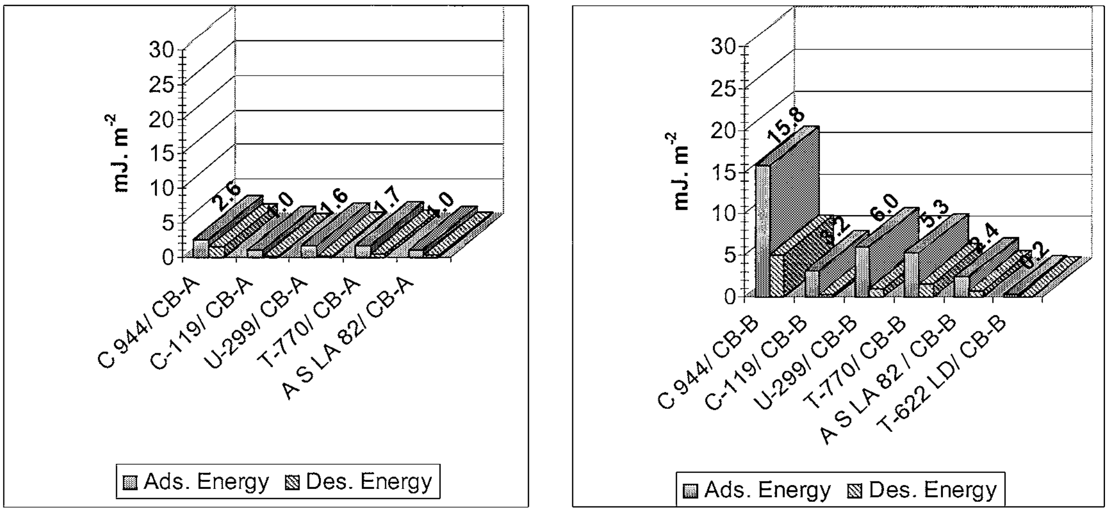
3.2. Adsorption behaviour of the HALS onto carbon black

Different stabilisers and carbon black pigments were chosen according to their chemical nature and surface features. CB-A and CB-B, both used in plastic applications, are studied with all the stabilisers chosen while for CB-C and CB-D their interaction with the Chimassorb 944® and Uvasil 299 LM® were examined in order to compare the different activity of the four black pigments with commercial stabilisers.

3.2.1. Overall adsorption activity

Adsorption and desorption energies resulting from the interactions of the different HALS with the carbon black pigments were estimated by the FMC procedure (Figs 3 and 4).

For CB-B and CB-A (Fig. 3) it was noticeable that Chimassorb 944® having a 4-2,2′,6,6′-tetramethylpiperidinyl-amino group showed a greater activity than Chimassorb 119® which has a more hindered 1,2,2′,6,6′-pentamethyl-4-piperidinyl)-amino structure. Investigations with model amines such as *sec*-butylamine, tributylamine and triethylamine show that 1° and 2° amines have a higher adsorption activity than 3° amines [6] . Chimassorb 944® has 2° amines in its side groups, whilst Chimassorb 119® does not. On the basis of the model compound study, it is



(CB-A) **(CB-B)**

Figure 3 Adsorption energy data for HALS on CB-A and CB-B.

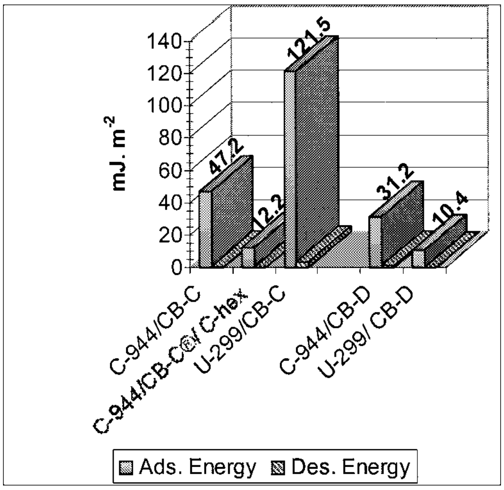


Figure 4 Adsorption energy data for HALS on CB-C and CB-D.

considered that the 2° amine side groups contribute to the higher adsorption activity of Chimassorb 944®. This activity can also be affected by the steric structure of these molecules. While Chimassorb 119® has a more branched structure that hinders the substituted amino groups, Chimassorb 944® has a more linear structure that allows closer access of its active groups to the carbon black surface.

The same explanation may be applied to the differing behaviour observed with Uvasil 299 LM® and Chimassorb 119®. However, it should be appreciated that the siloxane backbone and ether groups present will also contribute weakly to the overall interaction with carbon black. These interactions can enhance the overall activity of the Uvasil 299 LM® molecule.

Although Uvasil 299 LM® has a higher molar mass than Tinuvin 770®, both show similar activity as they interact with the same functional groups on carbon blacks CB-A and CB-B. Adsorption studies carried out using ethyl acetate show that ester groups interact weakly with carbon black [6], therefore the piperidine groups of Tinuvin 770® provide by far the largest contribution to its adsorption activity. The somewhat higher adsorption activity of Uvasil 299 LM® can be explained by dispersive interaction contributions from its siloxane backbone. Such interaction with the carbon black may be via the p–d π bonding system of the siloxane bonds and the π-electron clouds of the graphitic layers of the carbon black. The polymeric nature of the polysiloxane, together with its very high chain flexibility, will inevitably cause multi-point adsorption and hence a higher contribution to the overall adsorption activity than that of the ester grouping in Tinuvin 770®.

The behaviour shown by the ADEKSTAB LA 82® was close to that of Chimassorb 119®, and serves as confirmation that the main contribution to the overall adsorption activity is due to the (1,2,2′,6,6′-pentamethyl-4-piperidinyl)-amino structure.

The difference in the adsorption activities of the four carbon blacks towards the HALS further highlights the differences in the surface chemistry of the carbon blacks. The order of adsorption activity of the carbon blacks with the HALS can be ranked as follows:

With Chimassorb 944® and Uvasil 299 LM®, CB-C > CB-D > CB-B > CB-A.
Chimassorb 944®: (47.2 mJ m^{-2}) > (41.8 mJ m^{-2}) > (15.8 mJ m^{-2}) > (2.6 mJ m^{-2})
Uvasil 299 LM®: (121.5 mJ m^{-2}) > (107.7 mJ m^{-2}) > (6.0 mJ m^{-2}) > (1.6 mJ m-2)

Only CB-B and CB-A were studied with all of the HALS. The results show, in all the cases, that CB-B is more active than CB-A.

Due to the basic and nucleophilic character of the piperidine compounds and other amines present in HALS, the higher activity of a given carbon black could be due to a greater surface concentration of acidic adsorption sites on that particular carbon black. According to the literature [7] the presence of oxidised functional groups can be related to the volatile content of each carbon black, and hence their level of acidity [4, 5, 8, 9]. Thus, CB-C will have a greater surface concentration of acidic functional groups than CB-B, and CB-B greater than CB-A, as shown by the surface elemental compositions [1].

Although CB-D has the highest volatile content (8.5–12%), and hence the highest acidity when dispersed in water (pH of 2.5 ± 1), it nevertheless shows lower adsorption energies with Chimassorb 944® and Uvasil 299 LM® than CB-C. FTIR and XPS analysis (Table IV) confirms that CB-D is the most highly oxidised of the samples investigated [1] and the highest surface concentration of acidic functional groups [1]. This direct chemical evidence of the potentially more active surface of CB-D is at odds with the FMC data which shows CB-D to be less adsorption active than CB-C, which has roughly half the oxygen content of CB-D. This discrepancy could be explained by the existence of a "hydrogel effect" which is observed with highly functionalised polymers, e.g., polyvinylic alcohols. This effect occurs when the surface concentration of polar groups is beyond a certain critical level. Strong adsorption of atmospheric water molecules results in formation of a gel-like 3D network of hydrogen bonded water molecules, which effectively blocks off the adsorption sites to other adsorbates [10, 11]. In addition, strong mutual interactions between the closely adjacent functional groups can result in loss of adsorption activity. This effect will be most significant if the interactions between neighbouring surface groups are stronger than the interactions between the surface groups and the adsorbate molecules. Thus, the functionalities, which are believed to be at the edges of the graphitic basal planes of the carbon black, prefer interact with themselves, rather than the additives. It can be envisaged that a certain critical surface concentration of functional groups must be reached if the inter-group distance reduces sufficiently to allow mutual interaction, and hence loss of adsorption activity.

The chemical nature of surface functional groups must be also considered together with their concentration. CB-C has oxidised functional groups like SO_4 and C=O (carbonyls and carboxyls) whilst CB-B has mainly O-C and S-C (Table IV). The main functional groups on CB-B are O-C and S-C (alcohols, thiols, etc, as indicated by XPS analysis) [1]. The concentration of sulphates and sulphones is very low (10 times lower than the oxygen–carbon based groups). Their contributions to adsorption activity are probably not significant. Therefore, the difference between CB-A and CB-B can be justified by the difference of O-C and S-C concentration. This is consistent with the type and relative impurity of the oil feedstock used to produce CB-B, which has a higher sulphur content and oxidised hydrocarbon content than that used to produce CB-A. Taking into account the XPS analysis and the BET surface analysis, CB-B has a greater surface concentration of functional groups than CB-A and therefore a higher overall adsorption activity.

Porosity and surface topography are other factors to consider, and could potentially affect the adsorption of low and high molar mass adsorbates. Adsorption of piperidine and phenolic model compounds has been shown in the literature [12] to be affected by surface porsity. It can be envisaged that adsorption of polymers will also be affected, particularly by topological variations, such effects have been observed in the experimental data and are described below.

Trends in adsorption energy data for the polymeric HALS, Chimassorb 944® and Uvasil 299 LM®, highlight interesting differences in adsorption selectivity between the four carbon black samples. These differences are related partly to surface topography and the resultant effect on the entropy change of the polymeric backbone of the HALS during adsorption.

For CB-A and CB-B, the heat of adsorption (per unit area) of Chimassorb 944® is greater than Uvasil 299 LM® whilst for CB-C and CB-D, the reverse is true. On first examination this may imply that CB-C and CB-D have more selective groups towards the polysiloxane backbone of Uvasil 299 LM®. However, as both these HALS are polymeric; differences in configurational entropy can also explain the difference in selectivity of the carbon black surfaces towards these polymeric HALS. Heinrich *et al* [13] have described how the configurational entropy change of a polymer during adsorption is affected by surface topography. They found that with a dissordered surface, showing fractal geometry, the configurational entropy change is reduced relative to adsorption of the same polymer onto a flat surface of equal energy. In the latter case the entropy change will be negative (as increased order is being forced on the chain) therefore the enthalpy of adsorption will be reduced. In our case, CB-C and CB-D, are nitric acid treated carbon blacks, which according Table II and the literature [14] are more porous and therefore have rougher, more fractal-like, surface topography, than CB-A and CB-B. In this way, the flexible polysiloxane backbone of Uvasil 299 LM®, is able to fit into the surface features of these carbon blacks more easily than the more rigid carbon based backbone of Chimassorb 944® [15]. Together with the reduced entropy change, this more intimate contact will increase the enthalpic contribution from dispersive interactions between the polysiloxane chain and the carbon black surface, thus resulting in the higher heat of adsorption of Uvasil 299 LM® on CB-C and CB-D.

In the case of the less porous (i.e., smoother surface) CB-A and CB-B, the above entropic effect would be less significant, but may nevertheless work against adsorption of Uvasil 299 LM® more than Chimassorb 944®, as the latter may have a straighter and more rigid chain to start with. This may mean that the functionality of the carbon black surface and HALS becomes the more influential factor. Whilst both HALS are similar in terms of the 4-2,2′,6,6′-tetramethypiperidinyl-amino grouping, Uvasil 299 LM® lacks the 2° and 3° amine and triazine groups of Chimassorb 944®. Adsorption studies conducted by the authors using model amines [6] has indicated that such groupings will contribute strongly to adsorption activity. The triazine ring in Chimassorb 944® can also contribute to its adsorption activity, such a heterocyclic structure could interact with the CB basal graphene layers via van der Waals bonding. The presence of these additional groupings on Chimassorb 944® therefore explains its higher adsorption activity on CB-A and CB-B.

The difference between the adsorption and desorption energies can be related to the irreversibility of the adsorption mechanism and hence the degree of retention of the adsorbate on the surface. CB-C and CB-D showed stronger retention of the HALS than the other carbon blacks due to the strongly acidic, and microporous, surface of these samples. An increase in the magnitude of the difference between surface acidity and the basicity of the adsorbate, will result in stronger retention of the adsorbate [16]. Steric hindrance also affects such irreversibility, increased steric hindrance results in weaker retention (see Section 3.3).

Finally, it can be summarised from the discussion above that there are several factors affecting the adsorption of HALS onto carbon black:

(i) The presence and type of functional groups such as amines and esters.

(ii) Steric hindrance of functional groups, e.g., the steric hindrance of piperidine groups.

(iii) The conformational state/spatial structure of the molecule and flexibility of the backbone chain of polymeric HALS.

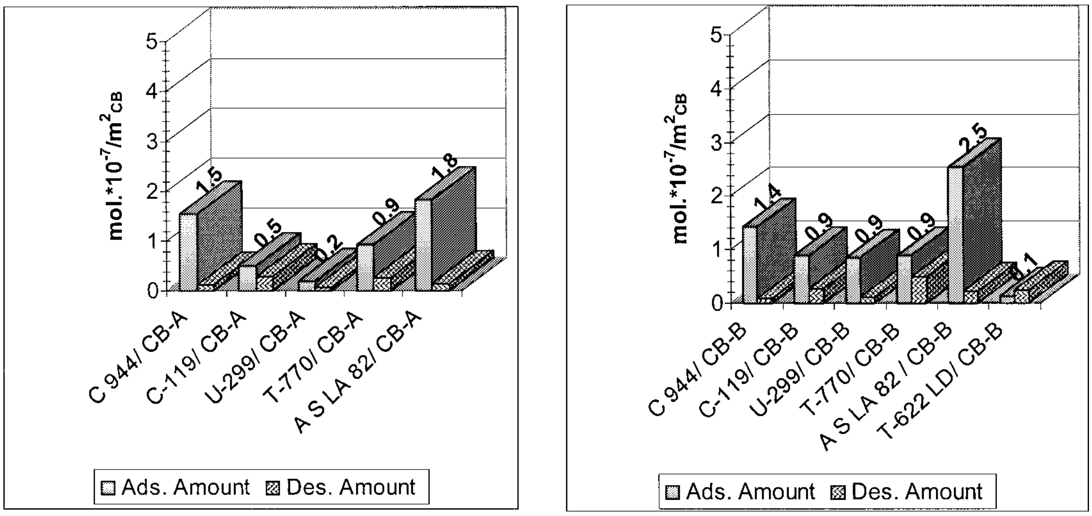
(iv) Carbon black surface topography, which is influenced by oxidising acid treatment, purity of the oil feed stock and graphitisation processes.

(v) Carbon black surface chemistry.

3.2.2. Amount of HALS adsorbed-desorbed

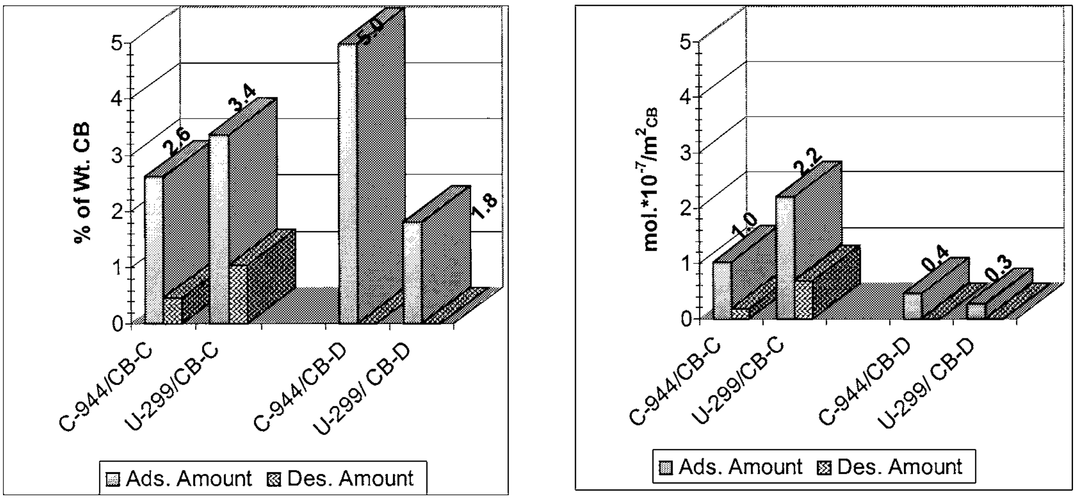
In general, the observed quantities adsorbed (Figs 5 and 6) can be related to the values of adsorption/desorption energy described previously and to the molar mass of probe. Thus, probes of high molar mass and high adsorption energy show the highest levels of adsorption.

With the notable exception of the Uvasil 299 LM®/CB-C system, Chimassorb 944® shows the highest mass percentage adsorption (4–5% w/w of CB) with all the carbon blacks followed by Chimassorb 119® and Uvasil 299 LM (Figs 5 and 6). These latter two



(CB-A) **(CB-B)**

Figure 5 Levels of HALS adsorbed and desorbed for CB-A and CB-B.



(CB-C and CB-D) **(CB-C and CB-D)**

Figure 6 Levels of HALS adsorbed and desorbed for CB-C and CB-D Amount (% w/w and mol m^{-2}).

polymeric HALS show similar levels of adsorption (1–1.5 % w/w) with CB-B. The remaining (monomeric) HALS, i.e., Tinuvin 770®, and ADKSTAB LA 82® show the lowest levels of adsorption (0.3–0.6% w/w of CB).

CB-C and CB-D are the most strongly adsorbing of the four carbon blacks investigated as they are the most acidic and have high surface porosity. Again, the trend seen in overall adsorption activity is repeated. For CB-D, CB-B and CB-A, Chimassorb 944®, adsorbs to the highest levels (5% w/w, 4.1% w/w, 1.8% w/w, respectively) followed by Uvasil 299 LM® (1.8% w/w, 1.2% w/w, 0.3% w/w, respectively). However, with CB-C the situation is reversed, and 3.4% w/w Uvasil 299 LM® is adsorbed compared with only 2.6% w/w Chimassorb 944®. This indicates that CB-C has a higher concentration of selective groups towards the polysiloxane backbone of Uvasil 299 LM®.

In general, for a given HALS, three factors influence the mass adsorbed. On one hand, a higher surface concentration of functional groups (with affinity towards the functional groups of the additive) will increase both the level and energy of adsorption. On the other hand, the specific surface area plays an obvious role as a carbon black with higher surface area will adsorb more additive than a chemically equivalent carbon black with lower surface area. Surface porosity is also a factor that cannot be ignored, generally a carbon black with higher porosity will adsorb more additive.

On the whole, the carbon black adsorption abilities can be ranked as follows:

With Chimassorb 944®, CB-D $>$ CB-B $\geq$ CB-A $>$ CB-C.
(5% w/w, 0.4 $\times$ 10^{-7} mol m^{-2}) $>$ (4.1% w/w, 1.4 $\times$ 10^{-7} mol m^{-2}) $>$ (4% w/w, 1.5 $\times$10^{-7} mol m^{-2}) $>$ (2.6% w/w, 1 $\times$10^{-7} mol m^{-2})
With Uvasil 299 LM®, CB-C $>$ CB-D $>$ CB-B $>$ CB-A.
(3.4% w/w, 2.2 $\times$10^{-7} mol m^{-2}) $>$ (1.8% w/w, 0.3 $\times$ 10^{-7} mol m^{-2}) $>$ (1.2% w/w, 0.9 $\times$10^{-7} mol m^{-2}) $>$ (0.3% w/w, 0.2 10^{-7} mol m^{-2})
With all the HALS, CB-B $>$ CB-A.

CB-D has the highest specific surface area (370 m^{2}g^{-1}) of the samples examined but Chimassorb

944® adsorbs on to this surface with lower energy (per unit area), however, by virtue of the high surface area, there will be a greater number of active adsorption sites per gram of CB-D. On the basis of the molar adsorption data, the latter sites will be less active and fewer in number, per unit area, than those of CB-C. Some of the CB-C adsorption sites contain carbonyl groups, detected by FTIR, together with others, such as phenolic and quinonic types. The overall contributions of all the functional groups present on the CB-C cause it to adsorb less Chimassorb 944® per unit area, than those of CB-B and CB-A. This effect cannot be explained by these latter two carbon blacks having a higher surface concentration of adsorption sites as this is not consistent with the XPS data. Therefore the mode of adsorption of the Chimassorb 944® must be being affected by the surface concentration and chemical nature of the adsorption sites. A high surface concentration of active adsorption sites is likely to cause flatter adsorption of Chimassorb 944®, with close multi-point attachment; whereas a low surface concentration of adsorption sites may result in loopy adsorption and in extreme cases attachment at only one end of the Chimassorb 944® chain. The former (flatter) mode of adsorption will result in a large adsorbate area and hence a low level of adsorption per unit area and high heat of adsorption. The latter mode of adsorption, however, will cause the adsorbate area to dramatically decrease and therefore give rise to a higher level of adsorption per unit area but reduced heat of adsorption. It can be envisaged that CB-C will adsorb Chimassorb 944® in a manner in which flat adsorption predominates; multiple interactions along the chain with the plentiful adsorption sites on the surface, cause the heat of adsorption to be high. CB-A and CB-B, with a lower surface concentration of adsorption sites, will promote loopy and/or end-tethered adsorption, therefore the level of adsorption per unit area will be higher than with CB-C.

XPS analysis clearly indicates that CB-C has a lower surface concentration of functional groups than CB-D [1], however, adsorption studies have revealed that CB-C has more active adsorption sites than CB-D. This is principally due to the hydrogel effect and mutual interaction between adjacent surface groups of CB-D, which significantly weakens their attraction to adsorbate molecules. These arguments are also shown to be correct on examination of the adsorption levels of Uvasil 299 LM®; CB-C adsorbs more of this HALS, with higher energy, than CB-D (Fig. 4).

CB-B adsorbs more HALS than CB-A, because of a greater amount per gram of active sites (higher overall adsorption activity), and this can be correlated to the XPS analyses and the volatile content [1]. This implies that whilst CB-B has a lower specific surface ($84\,m^2\,g^{-1}$) than CB-A ($130\,m^2\,g^{-1}$) the former must have a higher surface concentration of these functional groups.

Tinuvin 770®, ADKSTAB LA 82® and Tinuvin 622 LD® have both ester groups and piperidine structures as common features. The carbonyl groups of ester linkages can interact with carbon black surface groups (i.e., carboxylic acids (as on CB-C and CB-D) and phenolics) by hydrogen bonding. On the basis of model compound studies [6] we have found that the contribution of the ester group towards the overall energy of adsorption is not as significant as that from amines.

As expected, the difference between the amounts adsorbed and amounts desorbed can be related directly to the irreversibility of the adsorption mechanism. CB-C and CB- D showed a higher irreversibility (i.e., stronger retention of the HALS) than the other carbon blacks, because of their higher acidicity and micro-porous surfaces. The results showed that, in general, most of the adsorbed material was retained on the carbon black. For instance, 3–5% w/w Chimassorb 944® was retained on the four carbon blacks. Such an effect at first may seem alarming due to the possibility of effective loss of HALS from a formulation. However, this may not always be the case; controlled release of HALS from the filler surface could enhance the longevity of protection. Such effects have been shown to occur with silica in PE [17]. If however, stabiliser adsorption is deemed undesirable carbon blacks that do not adsorb stabilisers can be chosen.

3.3. Effect of the steric hindrance on the overall adsorption/desorption activity of piperidine model compounds

In order to explain how steric hindrance of the piperidine groups of HALS influences their adsorption/desorption behaviour, the adsorption characteristics of a range of piperidine model compounds, featuring varying degrees of steric hinderance, has been investigated, using CB-A and CB-B. Piperidine and ATMP were used as a model probes to investigate the effect of carbon black surface chemistry on adsorption activity. As usual the results of this study are presented as histograms showing adsorption and desorption data (energies and amounts) for each probe. Note that the sign of the exothermic adsorption energy has been reversed to aid comparison of the data.

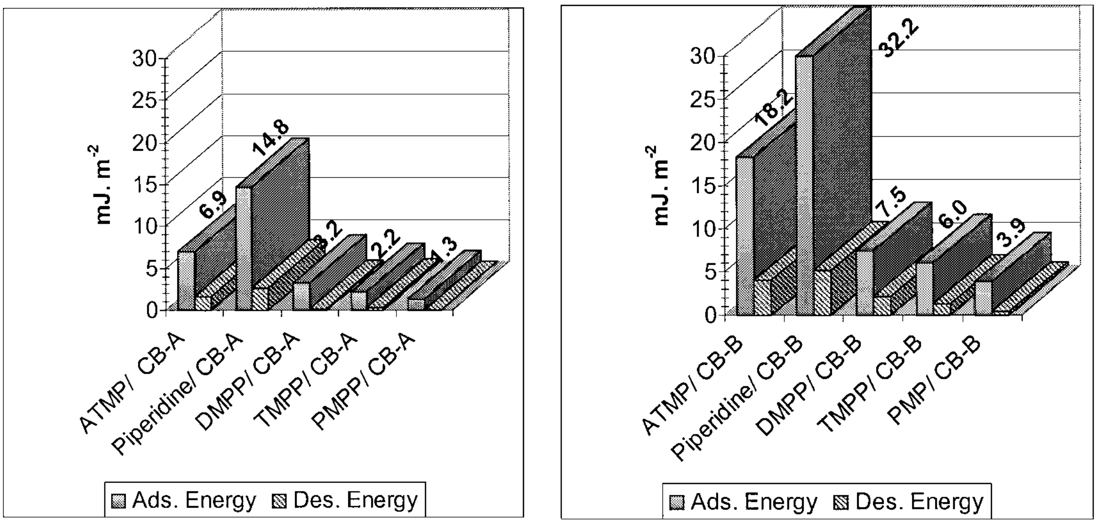
3.3.1. Overall adsorption activity

Piperidine, and ATMP gave identical trends in heat of adsorption per unit with all four carbon blacks (Figs 7 and 8). The activity of all the blacks with these additives can be ranked as follows:

$$\text{CB-C} > \text{CB-D} > \text{CB-B} > \text{CB-A}.$$

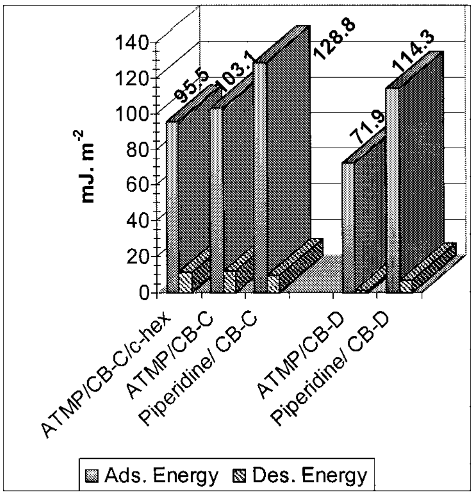
$$\text{Piperidine: } (128.8\ \text{mJ m}^{-2}) > (114.3\ \text{mJ m}^{-2})$$
$$> (32.2\ \text{mJ m}^{-2}) > (14.8\ \text{mJ m}^{-2})$$
$$\text{ATMP: } (95.5\ \text{mJ m}^{-2}) > (71.9\ \text{mJ m}^{-2})$$
$$> (18.2\ \text{mJ m}^{-2}) > (6.9\ \text{mJ m}^{-2})$$

As the results show (Fig. 7), it is evident that increasing steric hindrance of the piperidine group leads to a decrease in the overall adsorption/desorption activity of the model compounds studied with CB-A and CB-B. The adsorption activity reduces dramatically when 2,6-*cis*-dimethyl-piperidine is substituted for piperidine. Addition of two extra methyl groups to the 2 and 6



(CB-A) **(CB-B)**

Figure 7 Adsorption energy data for piperidine model compounds on CB-A and CB-B.



(CB-C and CB-D)

Figure 8 Adsorption energy data for piperidine model compounds on CB-C and CB-D.

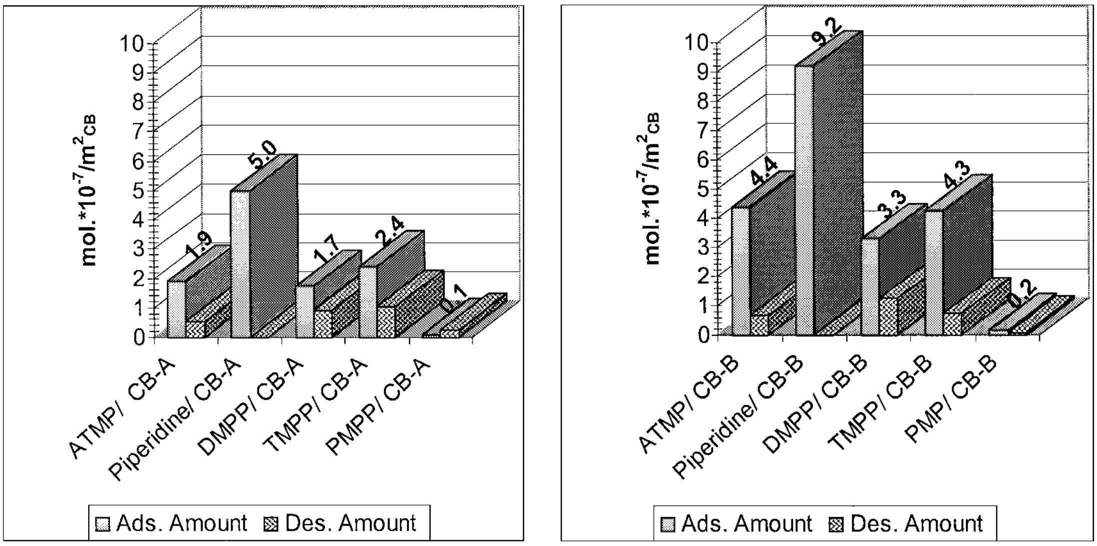
positions resulted in a less dramatic decrease in the overall adsorption activity. Finally, addition of a further methyl to the nitrogen (to give 1,2,2′,6,6′-pentamethyl-piperidine) resulted in a further decrease in the adsorption activity. The latter has an adsorption activity value close to that of other 3° amines with the same carbon black. For instance, with CB-B and CB-A, 1,2,2′,6,6′-pentamethyl-piperidine shows a value of 4.3 mJ m^{-2} and 3.9 mJ m^{-2}, respectively and triethylamine gives 7 mJ m^{-2} and 3.5 mJ m^{-2}, respectively.

The fact that 1,2,2′,6,6′-pentamethyl-piperidine adsorbs with lower energy than the tetramethyl species, verifies one of the assumptions made before concerning the different adsorption behaviour of some HALS. Chimassorb 119® (pentamethyl structure) adsorbs less than Chimassorb 944® (tetramethyl structure). It is interesting to note that with all the carbon blacks piperidine (2° amine) shows a higher adsorption/desorption activity than 4-Amino 2,2′,6,6′-tetramethyl-piperidine (ATMP), which contains a more nucleophilic 1° amine. This is likely to be due to the greater partial charge on the piperidine hydrogen, relative to the partial charge on the hydrogen of the 1° amine of the ATMP. In this way stronger hydrogen bonding can be formed by piperidine [16]. This observation may also be explained by the more basic character of 2° amines (i.e., piperidine pKa = 11.123) [18] relative to 1° amines (i.e., n-butylamine pKa = 10.77. By virture of its simple structure, piperidine can adopt a conformation that is conducive to more energetic interaction with the adsorption sites. With acidic carbon black surface groups such as carboxylic acid groups and phenols, the interaction with amines can be via both acid–base interaction and hydrogen bonding; whilst esters, quinones, lactones and other carbonyl compounds, interact with amines via hydrogen bonding only. Such interactions should be observed in the FTIR data, where carbonyl absorption frequency shifts to lower energies are observed. Overall trends in the adsorption activities of the carbon blacks are identical to those seen previously and can be thus explained in the same way.

Studies involving adsorption measurements from solution will always be bedevilled by solvent related effects. Such effects can be minimised by use of a solvent of just sufficient polarity to dissolve the adsorbate. In this study solvent effects were investigated via adsorption of ATMP and Chimassorb 944® on to CB-C from n-heptane and cyclohexane. From n-heptane, the heat of adsorption of ATMP was greater (103.1 mJ m^{-2}) than from cyclohexane (95.5 mJ m^{-2}) (Fig. 8). ATMP appears to be more strongly solvated by cyclohexane due to London interactions between the cyclic structures [18]. The same trend was also observed with Chimassorb 944®; from n-heptane the overall adsorption activity was greater (47.2 mJ m^{-2}) than from cyclohexane (12.2 mJ m^{-2}) (Fig. 5).

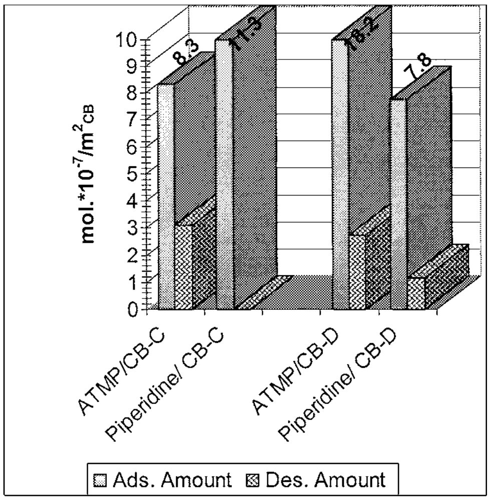
3.3.2. Amount of probe adsorbed-desorbed of model compounds

In general, the observed quantities bound (Figs 9 and 10) can be related to the previously described values of adsorption/desorption energy.



(CB-A) **(CB-B)**

Figure 9 Levels of model compound adsorbed and desorbed for piperidine model compounds on CB-A and CB-B.



(CB-C and CB-D)

Figure 10 Levels of model compound adsorbed and desorbed for piperidine model compounds on CB-C and CB-D.

The amounts of Piperidine and ATMP adsorbed can be ranked as follows:

With Piperidine,
CB-C > CB-B >CB-D > CB-A,
$(11.3 \times 10^{-7}\ \text{mol m}^{-2}) > (9.2 \times 10^{-7}\ \text{mol m}^{-2}) > (7.8 \times 10^{-7}\ \text{mol m}^{-2}) > (5 \times 10^{-7}\ \text{mol m}^{-2})$
and with ATMP,
CB-D > CB-C > CB-B > CB-A,
$(13.2 \times 10^{-7}\ \text{mol m}^{-2}) > (8.3 \times 10^{-7}\ \text{mol m}^{-2}) > (4.4 \times 10^{-7}\ \text{mol m}^{-2}) > (1.9 \times 10^{-7}\ \text{mol m}^{-2})$.

This indicates that with a primary amine such as ATMP, the level of adsorption is related to the surface concentration of functional groups, and hence to the oxygen content as indicated by the XPS analysis (Tables III and IV). This is clear evidence that the hydrogel effect, and mutual interactions between adjacent surface groups (associated with CB-D), can be overcome by a 1° amine but not by a 2° amine, such as piperidine. It may be that hydrogen bonding between the adjacent functional groups and the strongly adsorbed water molecules (constituting the hydrogel effect) is more effectively disrupted by a 1° amine. Thus, with piperidine the ranking is the same as that of ATMP, except in the case of CB-D. Furthermore, the fact the amount of pyridine adsorbed per unit area is greater than ATMP (an aliphatic 1° amine), may be related to the higher basicity of the former (piperidine group pKa = 11.123).

2,6-*cis*-dimethyl-piperidine, and 2,2′,6,6′-tetramethyl-piperidine show very similar levels of adsorption for each of carbon blacks examined. The level of adsorption of 1,2,2′,6,6′-pentamethyl-piperidine on both CB-B and CB-A is so low that it is below the limit of detection.

Generally speaking, the levels desorption of the amine model compounds are significantly less than the levels of adsorption, thus indicating strong retention on the carbon black surfaces. This trend is also reflected in the adsorption energy data and shows that adsorption of the amine model compounds, under the conditions selected, is generally irreversible.

Levels of adsorption of the amine model compounds are higher on CB-B than CB-A due to the higher surface concentration of adsorption sites, as confirmed by the XPS data. Although no clear trends are evident, the contribution of sulphur and nitrogen containing functional groups towards energies and levels of adsorption should not be ignored. The latter may become more significant if their concentration is relatively high.

3.4. FTIR studies on carbon black samples recovered from FMC cell

Carbon black samples recovered from the FMC cell after the adsorption-desorption processes, were analysed by transmission FTIR (as discs containing 0.09% w/w carbon black), together with the untreated carbon blacks and the additives alone. For each additive, the latter three spectra are stacked on the same set of axes to facilitate identification of vibrations associated with adsorbed stabiliser. Insight into the mode of adsorption

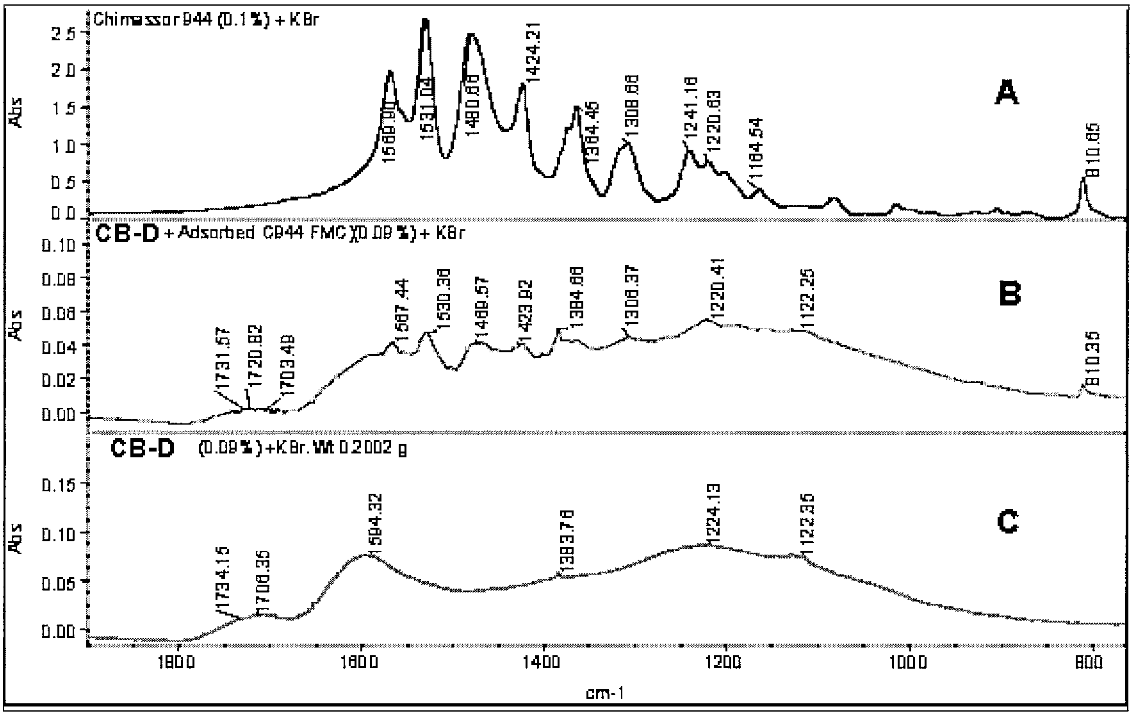


Figure 11 FTIR spectra of: (a) pure Chimassorb 944®, (b) CB-D modified with Chimassorb 944® in FMC, (c) pure CB-D carbon black.

can be acquired from absorption frequency shifts and broadening of absorption bands.

Adsorbed Chimassorb 944® is evident on all the CB samples analysed after treatment in the FMC cell. However, CB-A and CB-B showed only very weak vibration bands assignable to Chimassorb 944. Much stronger Chimassorb 944 vibration bands were observed with CB-C and CB-D. Data for CB-D only is shown to avoid duplication (Fig. 11). The IR absorptions from adsorbed Chimassorb 944® can be summarised as follows:

C-H stretching vibrations of CH_3 and CH_2 (centred at 2900 cm^{-1}) [not included in Fig. 11]

C-N deformations from 2° and 3° amines (at 1569 cm^{-1}, 1531 cm^{-1}, 1480 cm^{-1}, 1424 cm^{-1}, 1364 cm^{-1} and 1308 cm^{-1}),

N-H wagging in 2° amines (at 1221 cm^{-1} and 810 cm^{-1}).

In general, most of the Chimassorb 944® absorptions seem to be slightly shifted to lower frequencies, due to interaction with the adsorption sites on the carbon black surface (Fig. 11). The broad absorption band containing carbonyl vibrations (centred at 1595.0 cm^{-1}) would be expected to shift to lower energy if hydrogen bonding interaction occurred between carbon black

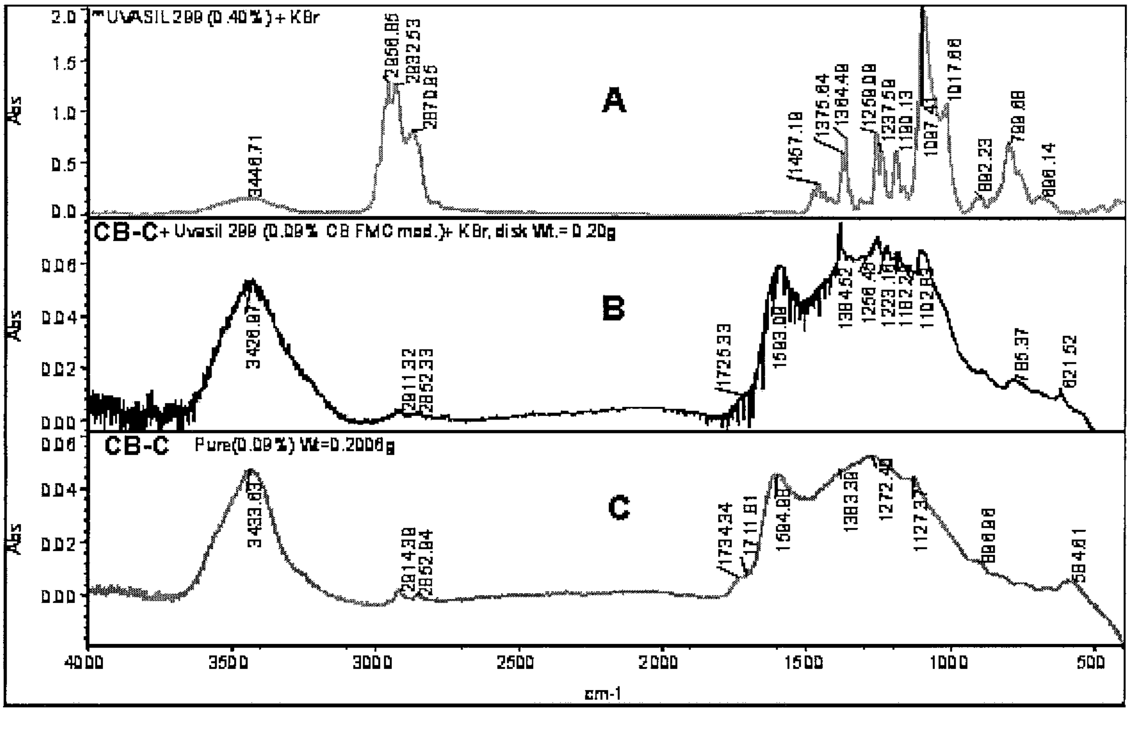


Figure 12 FTIR spectra of: (a) Uvasil 299 LM®, (b) CB-C modified with Uvasil 299 LM® in FMC, (c) pure CB-C carbon black.

surface carbonyl groups and the 2° amines and hindered piperidine groups of Chimassorb 944®. Such a shift can barely be resolved in Fig. 11 due to the breath of the band envelope and weak absorbance. Similar data was also obtained for Chimassorb 119® though the vibration bands were much weaker, reflecting a lower level of irreversible adsorption.

Absorptions from Uvasil 299 LM® are also detected on the carbon blacks, with CB-C and CB-D again showing the strongest vibration bands. Fig. 12 shows Uvasil 299 LM® adsorbed in the FMC onto CB-C. The principal vibrations can be listed as follows:

C-H stretching vibrations of CH_3 and CH_2 (centred at 2900 cm^{-1}),
C-O (alipatic ether), C-N (2° amine) and Si-O (siloxane) deformation vibrations (at 1259 cm^{-1}, 1237 cm^{-1}, 1190 cm^{-1} and 1097 cm^{-1}),
N-H wagging in secondary amines at 799 cm^{-1}.

Again, it is difficult to deduce the nature of interactions between the carbon black surface functional groups (i.e., carbonyl containing groups) and the piperidine and ether groupings of Uvasil 299 LM®, though hydrogen bonding is most probable form of interaction. In general most of the Uvasil 299 LM® absorptions (as with Chimassorb 944®) seem to be shifted a little to different frequencies, due to interactions with the carbon black surface (Fig. 12). The peak centred at 1097 cm^{-1} (C-O stretching vibrations of aliphatic ether and siloxane) shifts to higher frequencies, probably due to hydrogen bonding interaction.

4. Conclusions

FMC can be used to investigate the interactions between carbon black and HALS. The adsorption behaviour of HALS is heavily dependent on the molecular structure, particularly in terms of the number, type and degree of steric exposure of functional groups (i.e., amines, siloxanes, esters, etc). Other important aspects influencing adsorption behaviour include the spatial structure of the molecule and its conformational state, which in turn is influenced by the flexibility of the backbone. This factor is of particular significance with polymeric HALS, as the configurational entropy change during adsorption, and hence the heat of adsorption, will be affected.

It is evident that the chemical nature of the carbon black also plays a vital role in adsorption behaviour and is related to the presence of oxygen containing functional groups (detected by XPS and FTIR) and the concomitant variation in surface acidity. Selectivity towards specific HALS is dependent on the type, concentration and distribution of surface functional groups. This picture is further complicated by surface topography, which is affected by porosity and crystallinity.

The amounts of HALS adsorbed onto the carbon blacks, can be related to the values of adsorption/desorption energy described previously and to the molar mass of the HALS. Hence, probes with high molar mass and high activity generally show the greatest values of amounts adsorbed. It has also been shown that the level of adsorption appears to reach a maximum at a certain critical surface concentration of adsorption active functional groups. The mode of adsorption of polymeric HALS, in particular, had a strong influence on the level of adsorption, as the surface area of chain involved in adsorption interaction is proportional to the number of attachment points per chain.

It is evident that increasing steric hindrance of the piperidine group leads to a decrease in the energy of adsorption of piperidine model compounds. The more basic character of the a 2° amine relative to a 1° amine, and the simpler structure of piperidine results in a molecular conformation which is more conducive to energetic reaction with the surface functional groups of carbon black. This fact can shed some light on the way the HALS and the amine model compounds are adsorbed. With acidic carbon black surface groups as carboxylic acid groups and phenols the interaction can be by both via acid-base interaction and hydrogen bonding, whilst with esters, quinones, and lactones etc., hydrogen bonding has to be the main form of interaction.

According to our findings, and existing literature [2, 15], an adsorption equilibrium can be expected between the carbon black surface and the polymer matrix and that this can affect the photo and thermal stability performance of a given formulation. This study provides insight in to the possible nature of such equilibria.

Acknowledgements

The authors would like to thank to the Cabot Corporation for funding this work.

References

1. J. M. PEÑA, N. S. ALLEN, M. EDGE, C. M. LIAUW, F. SANTAMARÍA, O. NOISET and B. VALANGE, *J. Mater. Sci.* **36** (2001) 2885.
2. C. M. LIAUW, A. CHILDS, N. S. ALLEN, M. EDGE, K. R. FRANKLIN and D. G. COLLOPY, *Polym. Degrad. Stab.* **63** (1999) 391.
3. Cabot North American Technical Report S-136, Cabot-Corp, 1999.
4. H. P. BOEHM, *Carbon* **32** (1994) 759.
5. R. H. BRADLEY, I. SUTHERLAND and E. SHENG, *J. Colloid and Interface Sci.* **179** (1996) 561.
6. J. M. PEÑA, N. S. ALLEN, C. M. LIAUW, M. EDGE, B. VALANGE and F. SANTAMARÍA, *J. Mater. Sci.* **36** (2001) 4443.
7. J. B. DONNET, R. C. BANSAL and M. J. WANG, "Carbon Black Science and Technology" (Marcel Dekker, New York, 1993).
8. I. SUTHERLAND, E. SHENG, R. and H. BRADLEY, *J. Mat. Sci.* **31** (1996) 5651.
9. J. M. O'REILLY and R. A. MOSHER, *Carbon* **21** (1983) 47.
10. B. WESSLÉN and M. KOBER, *Biomaterials* **15** (1994) 278.
11. E. ÖSTERBERG and K. BERGSTRÖM, *Appl. Surface Sci.* **64** (1995) 197.
12. T. ASAKAWA, K. OGINO and K. YAMABE, *Bull. Chem. Soc. Jpn.* **58** (1985) 2009.
13. G. HEINRICH and T. A. VILGIS, *Rubber Chem. Technol.* **68** (1994) 26.
14. K. KAMEGAWA, K. NISHIKUBO and H. YOSHIDA, *Carbon* **36** (1998) 433.
15. V. MALATESTA, C. NERI, G. RANGHINO, L. MONTANARI and P. FANTUCCI, *Macromolecules* **26** (1993) 4287.
16. S. N. VINOGRADOV, "Hydrogen Bonding" (Van Nostrand Reinhold, New York and London, 1971).
17. C. M. LIAUW, A. CHILDS, N. S. ALLEN, M. EDGE, K. R. FRANKLIN and D. G. COLLOPY, *Polym. Degrad. Stab.* **65** (1999) 207.
18. K. PETER, C. VOLLHARDT and N. E. SCHORE, "Organic Chemistry," 2nd ed. (Freeman, New York, 1994).

Received 19 July 2000
and accepted 20 April 2001