HIGHLY HYDROPHOBIC *N*-ALKYLMALEIMIDE AND SUCCINIC ANHYDRIDE DERIVATIVES OF ANTHRACENE AS POTENTIAL SIZING AGENTS FOR THE PAPER INDUSTRY

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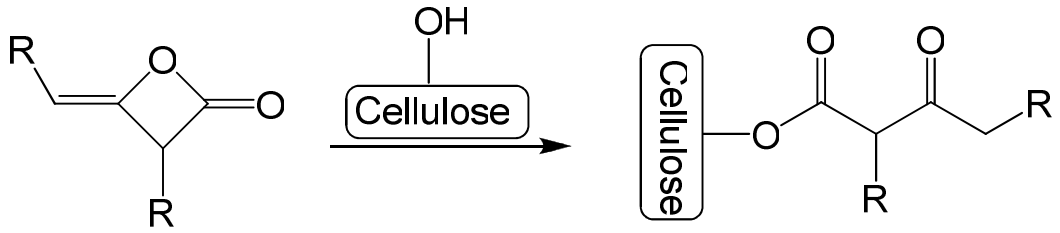
A series of *N*-alkylmaleimides and Diels-Alder adducts of anthracene have been prepared, converted into aqueous emulsions, and evaluated for their sizing properties through the production of paper handsheets. The sizing performance of each sample was compared to that of standard alkaline sizes, namely, alkenylsuccinic anhydrides (ASA). While none of the evaluated compounds was nearly as effective as the conventional ASA sizes, Diels-Alder adducts of anthracene with succinic anhydride moieties similar to that of ASAs appeared to display a totally different reactivity toward either the paper furnish or the hydroxyl group in alcohols tested during this study. This report shows that the presence of a high hydrophobic area and a succinic anhydride reactive moiety in a molecule does not guaranty a good paper sizing effect. This work also investigates and rationalizes the wide difference in reactivity between these two families of compounds, and provides some insights into the sizing mechanism of ASA paper sizing agents.

Keywords: *N*-alkylmaleimides, Diels-Alder adducts of anthracene, reactivity, alkenyl succinic anhydrides, paper sizing

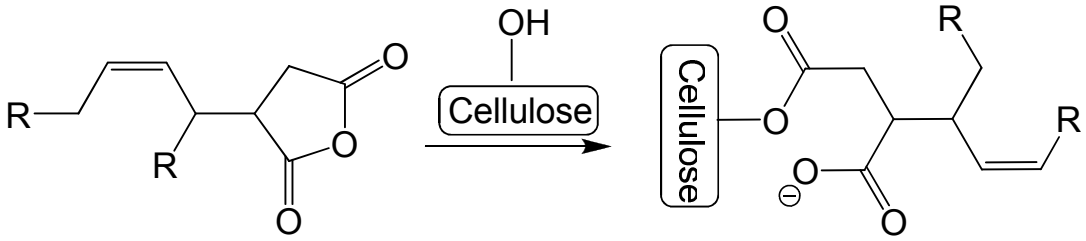
INTRODUCTION

The tendency of inks to feather when applied to paper surfaces led to the development of tub sizing practices as early as around 105 A.D., with animal glue being one of the first materials used for this purpose.[1,2]Surprisingly, only three major sizing agents have been developed for the paper industry so far: (1) the naturally occurring resin exuded from softwood known as oleoresin or gum rosin discovered in 1876, (2) the synthetic alkyl ketene dimer (AKD, **1**) developed in 1953, and (3) alkenyl succinic anhydride (ASA, **2**) first introduced as a paper sizing agent around 1974.[1,2] AKD and ASA still hold a major share of the internal sizing agents currently in use by the paper industry worldwide. However, there have been problems associated with the use of these sizing agents, including excessive use of size emulsion, poor size performance, problems with water contamination, poor retention, and formation of pitch deposits on machinery.[1-3] Despite significant improvements in printing technology, and mechanical advancement in papermaking, no major paper-sizing agent has been developed in recent years. More importantly, the mechanism by which current sizing agents achieve their effect is still a subject of contention. Despite compelling evidence of the formation of a covalent bond between the synthetic sizing agents above listed and the paper fibers (Schemes 1 and 2),[4-9] there have been some arguments among researchers regarding the exact nature of the interactions in this process.[5,10-15] Since the use of alum during the sizing process is also critical to the application of these synthetic agents to the surface of the wood fibers, critics have suggested that these sizing agents are retained at the surface of the paper furnish through electrostatic interactions, and have questioned the idea of the formation of covalent bonds process.[5,10-15] In fact, Hatanaka *et al*.[12] showed that it was possible to achieve effective sizing by using the diacid soap of ASA obtained from the hydrolysis of the succinic anhydride ring, in a similar manner as one would use rosin soap. In this report, a series of *N*-

alkylmaleimides, and Diels-Alder adducts of anthracene, having a succinic anhydride reactive end similar to that of ASAs, have been prepared and evaluated for their hydrophobizing properties, as well as for their internal sizing effects on paper handsheets. The mechanism by which these materials achieve their wetting resistance effects was investigated, using simple alcohols as a substitute prototype for the cellulosic paper fibers. This study also revealed some indirect insights into the mechanism by which ASAs achieve their sizing effects.



Scheme 1: Proposed reaction of AKDs with cellulose fibers



Scheme 2: Proposed reaction of ASAs with cellulose fibers

EXPERIMENTAL

Materials

All chemicals and solvents were purchased from major chemical suppliers, and were used without further purification unless stated otherwise. ASAs (Bersize® 7938T and 6936T), used as positive controls in the evaluation of the sizing properties of these compounds were provided by Bercen, a paper chemical manufacturer based in Denham Springs, Louisiana. The pulp used to make the handsheets was prepared from recycled paperboard, which was soaked overnight in enough water to produce a sample with a consistency of 3% pulp to water. The mixture was then defibered and run through a laboratory Valley Beater until the freeness of the pulp was between 400-475 CSF (measuredwith the Canadian Standard Freeness Tester).[16]

Spectroscopic data collection

NMR data were collected on a Bruker Ascend™-400 spectrometer operating at 400 MHz for ^{1}H and 100 MHz for ^{13}C. The concentration of all samples was 20 mg/0.5 mL of $CDCl_3$. The NMR data were recorded at 300 K, with chemical shifts (δ) reported in parts per million (ppm) relative to TMS (δH 0.00 and δC 0.0) used as the internal standard, or residual chloroform (δH 7.28 and δC 77.2), and coupling constants (*J*) in hertz. Compounds are characterized through one and two dimensional NMR data, including DEPTQ135, gradient-selected COSY60SW, gradient-selected HSQC (HSQCEDET) recorded in mode echo-antiecho, and gradient-selected HMBC (HMBCLPND) also recorded in mode echo-antiecho. As for X-ray crystallographic data collection, single crystals of various samples suitable for X-ray structure determination were mounted on the tip of a glass fiber using silicon grease, and intensity data were recorded on a STOE IPDS-2T diffractometer using graphite-monochromatedMoKα radiation (λ = 0.71073 Å). Supplementary crystallographic data for these compounds are deposited in the Cambridge Crystallographic Database and copies of these materials can be obtained free of charge from CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, http://www.ccdc.am.ac.uk., using the CCDC reference number provided in the characterization section of the corresponding compounds. Melting points were measured on a digital capillary melting point apparatus calibrated with benzoic acid (≥99.5%) [mp 122.38 °C (lit), obtained 122.4-122.6 °C]. Reaction mixtures were monitored using a 200-MS GC/MS Ion trap mass spectrometer or by TLC silica gel 60 F254 plates. Gravity and flash column chromatography were performed using type 60A silica gel (60-230 mesh).

Preparation and characterization of compounds

All the maleimide derivatives were prepared following a protocol previously reported by Wang *et al.*[17] To a suspension of maleic anhydride (1.1 eqv.) in toluene, a solution of long chain primary amine (1.0 eqv.) was added. The resulting mixture was stirred at 30 °C for 1 h after which, zinc bromide or zinc chloride (1.1 eqv.) and hexamethyldisilazane (1.5 eqv.) were added. The resulting suspension was heated under reflux for 2 h. After cooling to room temperature, the reaction mixture was poured into 0.5 M HCl solution. The organic layer was separated and the aqueous layer portion was extracted twice with ethyl acetate. The combined organic layer was washed with 2 portions of saturated aqueous solution of sodium bicarbonate, then with one portion of brine, dried over magnesium sulfate, and concentrated under reduced pressure to yield a viscous solid, which was purified on a silica gel column to produce the expected product.

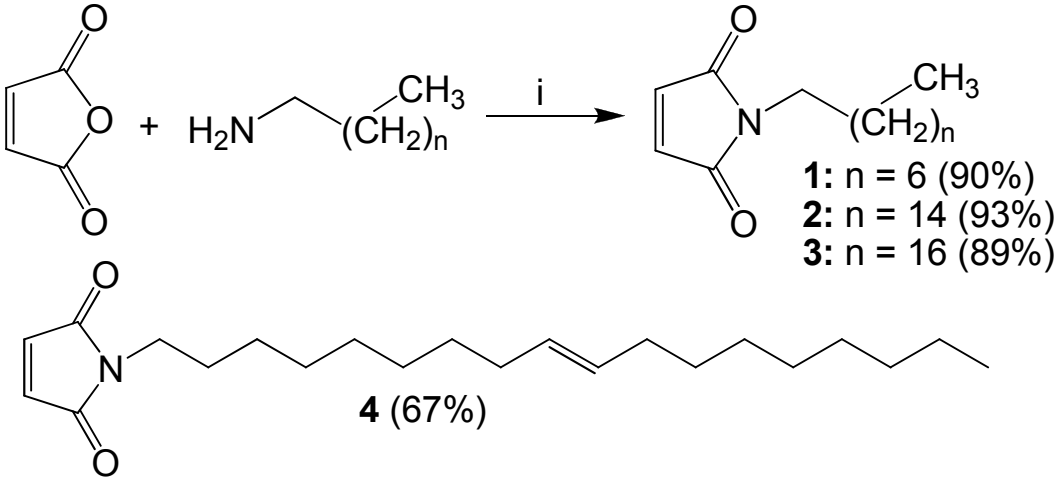
The structure of compounds **1** and **2** were confirmed by X-ray single crystal diffraction and the anisotropic representation of both compounds drawn at 50% probability level is shown in Figure 1.

1-Octylmaleimide(1)

This compound was obtained by reacting octylamine (50.0 g, 0.387 mol), maleic anhydride (41.7 g, 0.426 mol) in the presence of $ZnCl_2$ (58.0 g, 0.426 mol) and hexamethyl disilazane (93.7g, 0.580 mol) as described above to yield, after purification on a silica gel column using a mixture of hexanes-dichloromethane (7:3), **1** (56.2 g, 90%) as clear oil that crystallizes upon standing (mp 39.5-40.1 ^{o}C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.87 (3H, t, J = 6.8 Hz), 1.26-1.28 (10H, m), 1.56-1.59 (2H, m, J = 6.8 Hz), 3.51 (2H, t, J = 6.8 Hz), 6.69 (2H, s). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.1, 22.6, 26.8, 28.6, 29.1, 29.2, 31.8, 38.0, 134.0, 171.9. HRESI-MS: $[M + H]^+$*m/z* 210.14748 (calcd. 210.1489 for $C_{12}H_{20}NO_2$). The structure of this compound was confirmed by X-ray single crystal diffraction. Crystal data: $C_{12}H_{19}NO_2$, M_r = 209.28 g/mol, Monoclinic space group P1 21/c1, a= 15.608(3) Å,b = 7.4262(15) Å, c = 10.730(2) Å, β = 105.30(3)°, V = 1199.61(985) Å^3, T = 90 K, Z = 4, D_x = 1.1587 g/cm^3, θ_{max} = 32.5° (Cu $K\alpha$). The crystal structure data are deposited at the Cambridge Crystallographic Data Centre (CCCDC 1049537).

1-Hexadecylmaleimide (2)

This compound was obtained by reacting hexadecylamine (50.0 g, 0.207 mol), maleic anhydride (22.3 g, 0.228 mol) in the presence of $ZnBr_2$ (51.3 g, 0.228 mol) and hexamethyl disilazane (50.1 g, 0.311 mol) as described above to yield, after purification on a silica gel column using a mixture of hexanes-dichloromethane (7:3), **2** (61.9 g, 93%) as clear oil that crystallizes upon standing (mp = 69.1-70.2 ^{o}C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88 (3H, t, J = 6.8 Hz), 1.25 (26H, m), 1.58 (2H, m), 3.51 (2H, t, J = 7.2 Hz), 6.69 (2H, s). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.2, 22.7, 26.8, 28.6, 29.2, 29.4, 29.5, 29.6, 29.7, 29.8, 29.0, 31.9, 37.9, 134.1, 170.9. HRESI-MS: $[M + H]^+$*m/z* 322.27640 (calcd. 322.2741 for $C_{20}H_{36}NO_2$). The structure of this compound was confirmed by X-ray single crystal diffraction. Crystal data: $C_{20}H_{35}NO_2$, M_r = 321.49 g/mol, Monoclinic space group P1 21/c1, a= 23.975(5) Å,b = 7.3576(15) Å, c = 10.825(2) Å, β = 93.83(3)°, V = 1905.25(388) Å^3, T = 293 K, Z = 4, D_x = 1.12072 g/cm^3, θ_{max} = 25.02° (Cu $K\alpha$). The crystal structure data are deposited at the Cambridge Crystallographic Data Centre (CCDC 1498860).



Scheme 3: Preparation of *N*-alkylmaleimide derivatives (reagents: $ZnBr_2$, hexamethyldisilazane, Toluene, reflux for 2 h)[17]

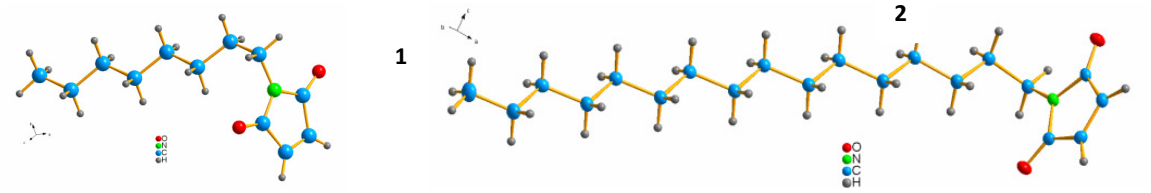
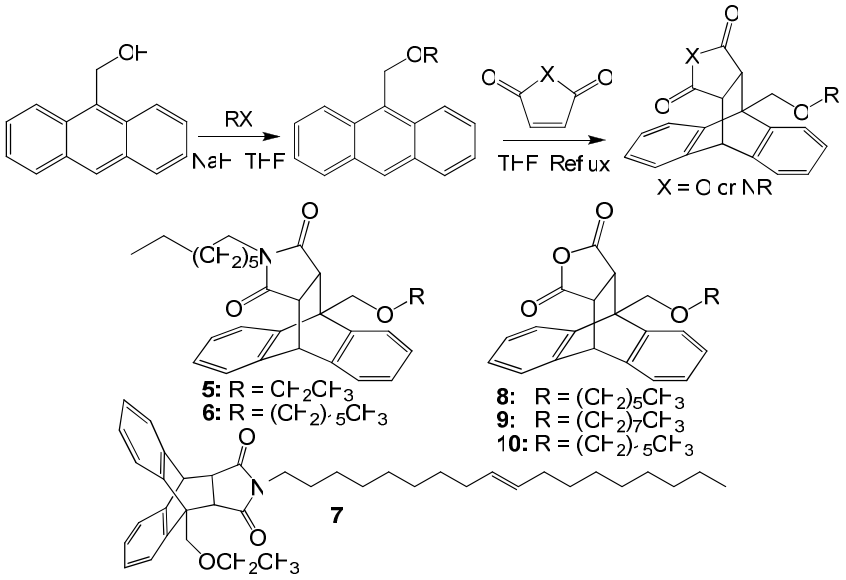


Figure 1: Anisotropic representation of **1** and **2** drawn at 50% probability level

1-Octadecylmaleimide (3)

This compound was obtained by reacting octadecylamine (50.0 g, 0.186 mol), maleic anhydride (20.0 g, 0.204 mol) in the presence of $ZnBr_2$ (45.96 g, 0.204 mol) and hexamethyl disilazane (44.9 g, 0.278 mol) as described above to yield, after purification on a silica gel column using a mixture of hexanes-dichloromethane (7:3), **3** (57.7 g, 89%) as clear oil that crystallizes upon standing (mp = 62.3-64.5 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88 (3H, t, *J* = 6.8 Hz), 1.25 (30H, m), 1.57 (2H, m, *J* = 6.8 Hz), 3.51 (2H, t, *J* = 7.2 Hz), 6.68 (2H, s). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.1, 22.7, 26.8, 28.6, 29.2, 29.4, 29.5, 29.6, 29.7, 29.8, 29.9, 31.9, 37.9, 134.2, 170.9. HRESI-MS: $[M + H]^+$*m/z* 350.27000 (calcd. 350.3054 for $C_{22}H_{40}NO_2$).



Scheme 4: Synthesis of maleimide or anhydride Diels-Alder adducts of anthracene and derivatives

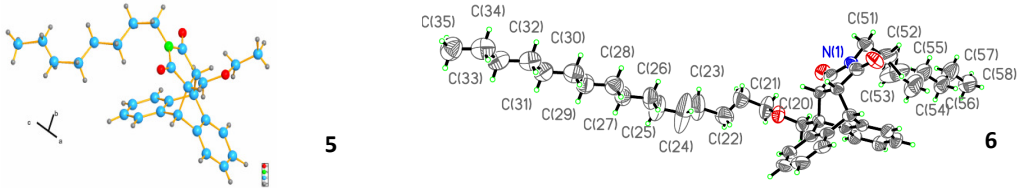


Figure 2: Anisotropic representation of **5** and **6** drawn at 50% probability level

(E)-1-(Octadec-9-enyl)maleimide (4)

This compound was obtained by reacting oleylamine (35.0 g, 0.131 mol), maleic anhydride (14.1 g, 0.144 mol) in the presence of $ZnCl_2$ (19.6 g, 0.144 mol) and hexamethyldisilazane (31.7 g, 0.196 mol) as described above to yield, after purification on a silica gel column using a mixture of hexanes-dichloromethane (7:3), **4** (30.5 g, 67%) as clear oil. ^{1}H

NMR (400 MHz, $CDCl_3$) δ 0.82 (3H, t, *J* = 7.2 Hz), 1.19-1.23 (22H, m), 1.50-1.57 (2H, m), 1.92-1.99 (4H, m), 3.47 (2H, t, *J* = 7.2 Hz), 5.29-5.34 (2H, m), 6.64 (2H, s). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.3, 22.9, 27.0, 27.3, 27.4, 28.7, 29.4, 29.5, 29.6, 29.9, 30.0, 31.9, 32.1, 32.7, 32.8, 38.1, 130.0, 130.1, 134.2, 171.0. HRESI-MS: $[M + H]^+$ *m/z* 348.29400 (calcd. 348.2897 for $C_{22}H_{38}NO_2$).

As for the Diels-Alder adducts, they were obtained by reacting 9-anthracenemethanol alkylated through a Williamson reaction, with some of the above listed *N*-alkylmaleimide derivatives, as well as with maleic anhydride, as illustrated in Scheme 4. The obtained reaction mixture was then concentrated under reduced pressure and purified over a silica gel column using a mixture of hexanes-dichloromethane to produce the desired product.

A total of six Diels-Alder adducts were prepared, and their structures are shown in Scheme 4. The structure of compounds **5** and **6** were confirmed by single crystal X-ray diffraction, and Figure 2 shows the anisotropic representation of these compounds drawn at 50% probability level.

N-Octyl-1-ethoxymethyl-dibenzo[e,h]bicyclo[2,2,2]octane(2,3)dicarboximide (5)

This compound was obtained by refluxing 9-(ethoxymethyl)anthracene (2.16 g, 9.14 mmol) with 1-octylmaleimide (1.91, 9.14 mmol) in THF overnight (18 hours). The mixture was then concentrated under reduced pressure, and the residue purified on a silica gel column using a mixture of hexanes-ethyl acetate (9:1) to yield **5** (3.67 g, 90.1%) as a yellowish oil that crystallizes upon standing (mp 80.0-82.4 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.76 (2H, q*, *J* = 7.2 Hz), 0.80 (2H, q*, *J* = 7.4 Hz), 0.88 (3H, t, *J* = 6.8 Hz), 1.05 (2H, m), 1.16 (2H, m), 1.18 (2H, m), 1.29 (2H, m), 1.38 (3H, t, *J* = 7.2 Hz), 3.06 (2H,t, *J* = 7.6 Hz), 3.19 (1H, dd, *J* = 8.4, 6.8 Hz), 3.31 (1H, d, *J* = 8.4 Hz), 3.91 (2H, q, *J* = 7.2 Hz), 4.72 (1H, d, *J* = 6.8 Hz), 4.76 (1H, d, *J* = 1.2 Hz), 4.80 (1H, d, *J* = 1.2 Hz), 7.09-7.11 (2H, m), 7.13 (1H, dd, *J* = 8.4, 1.8 Hz), 7.16 (1H, dd, *J* = 8.4, 7.2 Hz), 7.20 (1H, dd, *J* = 8.8, 7.2 Hz), 7.27 (1H, dd, *J* = 8.0, 1.2 Hz), 7.33 (1H, dd, *J* = 8.8, 1.7 Hz), 7.56 (1H, dd, *J* = 7.2, 2.1 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ:14.1, 15.4, 22.7, 26.5, 27.2, 28.9, 29.0, 31,8, 38.5, 45.9, 47.7, 67.2, 67.5, 122.2, 123.6, 124.2, 125.2, 126.4, 126.5, 126.7, 126.8, 139.0, 139.4, 142.2, 142.3, 176.2, 176.9. HRESI-MS: $[M + H]^+$ *m/z* 446.27315 (calcd. 446.2690 for $C_{29}H_{36}NO_3$). (q* = quintet). The structure of this compound was confirmed by X-ray single crystal diffraction. Crystal data: $C_{29}H_{35}NO_3$, M_r = 445.58 g/mol, triclinic space group P-1, *a* = 11.137(2) Å, *b* = 11.184(2) Å, *c* = 11.502(2) Å, α = 93.16(3)°, β = 100.04(3)°, γ = 115.20(3)°, *V* = 1262.92(40) Å^3, T = 293 K, *Z* = 2, D_x = 1.17166 g/cm^3, θ_{max} = 24.93° (Cu *K*α). The crystal structure data are deposited at the Cambridge Crystallographic Data Centre (CCDC 1052505).

N-Octyl-1-hexadecyloxymethyl-dibenzo[e,h]bicycle [2,2,2]octane(2,3)dicarboximide (6)

This compound was obtained by refluxing 9-(hexadecyloxymethyl)anthracene (19.2 g, 44.4 mmol) with 1-octylmaleimide (9.29 g, 44.4 mmol) in THF overnight (18 hours). The mixture was then concentrated under reduced pressure, and the residue purified on a silica gel column using a mixture of hexanes-ethyl acetate (9.5:0.5) to yield **6** (20.6 g, 72.4%) as a yellowish oil that crystallizes upon standing (mp 57.1-57.7 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.74 (2H, q*, *J* = 7.2 Hz), 0.81 (2H, q*, *J* = 7.6 Hz), 0.88 (6H, t, *J* = 7.2 Hz), 1.07 (2H, m), 1.15 (2H, m), 1.22-1.31 (28H, m), 1.45 (2H, q*, *J* = 6.8 Hz), 1.73 (2H, q*, *J* = 6.8 Hz), 3.07 (2H, t, *J* = 7.6 Hz), 3.20 (1H, dd, *J* = 8.4, 3.2 Hz), 3.23 (1H, d, *J* = 6.8 Hz), 3.83 (2H, m), 4.72 (1H, d, *J* = 2.8 Hz), 4.76 (1H, d, *J* = 9.6 Hz), 4.81 (1H, d, *J* = 9.2 Hz), 7.07-7.14 (3H, m), 7.17 (1H, d, *J* = 6.4 Hz), 7.23 (1H, d, *J* = 6.9 Hz), 7.26 (1H, t, *J* = 6.4 Hz), 7.34 (1H, d, *J* = 7.2 Hz), 7.55 (1H, d, *J* = 7.6 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ:14.2, 22.6, 22.7, 26.4, 26.5, 27.1, 28.9, 29.0, 29.3, 29.4, 29.5, 29.7, 29.8, 29.9, 31.8, 31.9, 38.4, 45.8, 47.7, 48.8, 67.7, 71.9, 122.2, 123.6, 124.3, 125.1, 126.3, 126.4, 126.7, 126.8, 139.0, 139.4, 142.2, 142.3, 176.1, 177.0.HRESI-MS: $[M + H]^+$ *m/z* 642.48048 (calcd. 642.4881 for $C_{43}H_{64}NO_3$). (q* = quintet). The structure of this compound was confirmed by X-ray single crystal diffraction. Crystal data: $C_{43}H_{63}NO_3$, M_r = 641.94g/mol, triclinic space group P-1, *a* = 9.5126(4)Å, *b* = 10.8987(4) Å, *c* = 19.8855(7) Å, α = 82.155(2)°, β = 85.380(2)°, γ = 71.930(3)°, *V* = 1940.00(13) Å^3, T = 296(2)K, *Z* = 2, D_x = 1.099 g/cm^3, θ_{max} = 47.65° (Cu *K*α). The crystal structure data are deposited at the Cambridge Crystallographic Data Centre (CCDC 1498861).

N-(E)-(Octadec-9-enyl)-1-hexadecyloxymethyl dibenzo[e,h]bicyclo[2,2,2]octane(2,3)dicarboximide (7)

This compound was obtained by refluxing 9-(ethoxymethyl)anthracene (7.34 g, 31.1 mmol) with (*E*)-1-(Octadec-9-enyl) maleimide (10.8 g, 31.1 mmol) in THF overnight (18 hours). The mixture was then concentrated under reduced pressure, and the residue purified on a silica gel column using a mixture of hexanes-ethyl acetate (9:1) to yield **7** (15.8 g, 87.3%) as a yellowish oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: ^{13}C NMR (100 MHz, $CDCl_3$) δ: 0.75 (2H, q*, *J* = 7.2 Hz), 0.82 (2H, q*, *J* = 7.6 Hz), 0.88 (3H, t, *J* = 6.8 Hz), 1.07 (2H, m), 1.18 (2H, m), 1.21-1.31 (16H, m), 1.39 (3H, t, *J* = 6.8 Hz), 2.01 (4H, m), 3.07 (2H, t, *J* = 6.8 Hz), 3.21 (1H, dd, *J* = 8.4, 3.2 Hz), 3.33 (1H, d, *J* = 7.2 Hz), 3.92 (2H, m), 4.73 (1H, d, *J* = 3.2 Hz), 4.78 (1H, d, *J* = 9.2 Hz), 4.83 (1H, d, *J* = 9.2 Hz), 5.37 (2H, m), 7.08-

7.14 (3H, m), 7.17 (1H, d, *J* = 7.6 Hz), 7.20 (1H, d, *J* = 7.2 Hz), 7.27 (1H, dd, *J* = 6.4, 3.6 Hz), 7.34 (1H, d, *J* = 6.8 Hz), 7.56 (1H, d, *J* = 7.6 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 14.1, 15.3, 22.7, 26.4, 26.9, 27.2, 29.2, 29.5, 29.8, 31.9, 38.4, 45.8, 47.6, 48.7, 67.1, 67.5, 122.2, 123.6, 124.2, 125.1, 126.4, 126.5, 126.7, 126.8, 129.8, 130.0, 134.0, 139.0, 139.3, 142.2, 142.4, 176.2, 177.0. HRESI-MS: $[M + H]^+$ *m/z* 584.40911 (calcd. 584.4098 for $C_{39}H_{54}NO_3$). (q* = quintet).

1-Hexyloxymethyl-dibenzo[e,h]bicyclo[2,2,2] octane(2,3)succinic anhydride (8)

This compound was obtained by refluxing 9-(hexyloxymethyl)anthracene (8.03 g, 27.5 mmol) with maleic anhydride (2.69 g, 27.5 mmol) in THF overnight (18 hours). The mixture was then concentrated under reduced pressure, and the residue purified on a silica gel column using a mixture of hexanes-dichloromethane (1:1) to yield **8** (9.36 g, 87.3%) as transparent crystals (mp 164.1-164.5 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.91 (3H, t, *J* = 6.8 Hz), 1.32 (2H, m), 1.35 (2H, m), 1.46 (2H, m), 1.73 (2H, q*, *J* = 6.4 Hz), 3.51 (1H, dd, *J* = 9.2, 9.6 Hz), 3.68 (1H, d, *J* = 9.2 Hz), 3.83 (2H, t, *J* = 6.4 Hz), 4.69 (1H, d, *J* = 9.6 Hz), 4.74 (1H, d, *J* = 2.3 Hz), 4.76 (1H, d, *J* = 2.3 Hz), 7.11-7.14 (2H, m), 7.13-7.17 (2H, m), 7.22 (1H, dd, *J* = 8.4, 2.3 Hz), 7.31 (1H, dd, *J* = 8.6, 2.4 Hz), 7.33 (1H, dd, *J* = 8.4, 1.9 Hz), 7.53 (1H, dd, *J* = 7.6, 1.8 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 14.0, 22.7, 26.0, 29.7, 31.6, 45.6, 46.8, 48.6, 48.7, 66.9, 72.0, 122.2, 123.8, 124.3, 125.3, 126.7, 126.8, 127.4, 127.5, 138.4, 138.8, 141.4, 141.5, 169.39. 170.7. HRESI-MS: $[M + H]^+$ *m/z* 391.1911 (calcd. 391.1904 for $C_{25}H_{27}O_4$). (q* = quintet).

1-Octyloxymethyl-dibenzo[e,h]bicyclo[2,2,2]octane(2,3)succinic anhydride (9)

This compound was obtained by refluxing 9-(octyloxymethyl)anthracene (3.71 g, 11.6 mmol) with maleic anhydride (1.14 g, 11.6 mmol) in THF overnight (18 hours). The mixture was then concentrated under reduced pressure, and the residue purified on a silica gel column using a mixture of hexanes-dichloromethane (1:1) to yield **9** (4.33 g, 89.3%) as a white powder (mp 131.4-131.6 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.89 (3H, t, *J* = 6.4 Hz), 1.30 (2H, m), 1.38 (2H, m), 1.39 (2H, m), 1.44 (2H, m), 1.47 (2H, m), 1.74 (2H, q*, *J* = 6.4 Hz), 3.43 (1H, dd, *J* = 9.2, 9.6 Hz), 3.60 (1H, d, *J* = 9.2 Hz), 3.83 (2H, d, *J* = 6.4 Hz), 4.67 (1H, d, *J* = 9.6 Hz), 4.72 (1H, d, *J* = 2.1 Hz), 4.73 (1H, d, *J* = 2.1 Hz), 7.12-7.17 (4H, m), 7.18 (1H, dd, *J* = 7.8, 2.0 Hz), 7.28 (1H, dd, *J* = 8.4, 1.8 Hz), 7.30 (1H, dd, *J* = 8.2, 2.0 Hz), 7.52 (1H, dd, *J* = 7.2, 1.8 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 14.1, 22.6, 26.3, 29.3, 29.4, 29.7, 31.8, 45.6, 46.8, 48.6, 48.6, 66.9, 72.0, 122.1, 123.8, 124.3, 125.3, 126.8, 126.7, 127.4, 127.4, 138.4, 138.8, 141.4, 141.5, 169.4, 170.7. HRESI-MS: $[M + H]^+$ *m/z* 419.2226 (calcd. 419.2217 for $C_{27}H_{31}O_4$). (q* = quintet).

1-Hexadecyloxymethyl-dibenzo[e,h]bicyclo [2,2,2]octane(2,3)succinic anhydride (10)

This compound was obtained by refluxing 9-(hexadecyloxymethyl)anthracene (13.0 g, 30.0 mmol) with maleic anhydride (2.95 g, 30.0 mmol) in THF overnight (18 hours). The mixture was then concentrated under reduced pressure, and the residue purified on a silica gel column using a mixture of hexanes-ethyl acetate (9:1) to yield **10** (12.9 g, 80.9%) as a yellowish powder (mp 109.1-110.3 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.88 (3H, t, *J* = 6.8 Hz), 1.21-1.37 (24H, m), 1.43 (2H, q*, *J* = 7.2 Hz), 1.74 (2H, q*, *J* = 7.6 Hz), 3.54 (1H, dd, *J* = 9.2, 3.2 Hz), 3.72 (1H, d, *J* = 9.6 Hz), 3.83 (2H, t, *J* = 6.4 Hz), 4.69 (1H, d, *J* = 9.6 Hz), 4.76 (2H, m), 7.15-7.24 (5H, m), 7.32-7.33 (2H, m), 7.53 (1H, dd, *J* = 7.6, 2.1 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 14.1, 22.7, 26.4, 29.4, 29.5, 29.6, 29.7, 29.8, 31.9, 45.6, 46.9, 48.6, 48.7, 66.9, 72.0, 122.2, 123.8, 124.3, 125.4, 126.7, 126.8, 127.5, 127.5, 138.4, 138.8, 141.4, 141.5, 169.4, 170.8. HRESI-MS: $[M + H]^+$ *m/z* 531.35318 (calcd. 531.3469 for $C_{45}H_{47}O_4$). (q* = quintet).

Evaluation of the paper sizing properties

As a quick test for hydrophobicity, each of the compounds above described were evaluated using the blotter assay, also known as water-drop-absorption assay, which measures the time required for droplets of water to be absorbed by a sheet of paper with the surface coated with the sample to be evaluated. In this assay, each sample displayed similar or superior hydrophobicity when compared to that of the standard ASA sizing agent. These results are consistent with the large hydrophobic surfaces present by design in each of these compounds.

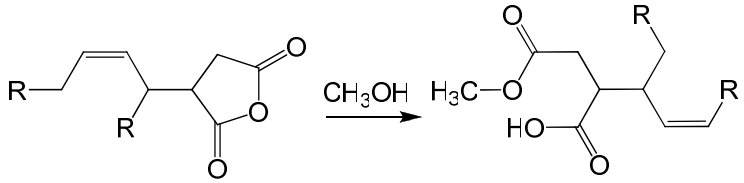
As for the evaluation of the internal sizing properties of these compounds on a paper handsheet, two main techniques were used: the Hercules photosize size test (HST) and the Cobb size test (CST). The Hercules size test (HST; Tappi Method T530) measures the decrease in reflectance of the opposite side of a sheet of paper internally sized with the sample being evaluated, and covered with a given amount of ink. In this assay, the time (in seconds) for a freshly prepared green 1% formic acid dye ink to penetrate a handsheet until the obtained reflectance is 80% of the original value, is measured.[18-19] The HST (Model KC or KA) measures the reflectance using a photocell. Handsheets were made from a pulp of freeness number 424, the size contained 0.8% active DOSS surfactant, at a grammage of 100g/m^2, using Floquip Handsheet Former Model Number: Floquip Form US 1A STD. The results reported in Table 1 represent the average of each test, run in triplicates.

On the other hand, the Cobb size test (CST) measures the amount of water (in g water/m²) absorbed by a given area of a paper sheet treated with sizing agent being evaluated, in a specified amount of time (usually 1 to 2 minutes).[20-22]

Table 1
Data obtained from the evaluation of samples **1-10** using both the HST and CST techniques

Samples	Melting points (°C)	Grammage	Mean particle size (µm)	Particle diameter (% <2 µm)	COV	HST[a] (seconds)	Cobb test[b] (wt GSM)
Blank[a]	-		-	-	-	0.583	179
Bersize 6936[b] (C_{16} – ASA)	liquid at RT*	100.7	0.797	98.7	45.3	1125.3	31.0
Bersize 7938[b] (C_{18} – ASA)	liquid at RT	102.1	0.867	98.1	45.0	1200.0	18.0
1	39.5-40.1	100.7	10.28	9.6	47.2	0.4	475
2	69.1-70.2	101.2	6.56	45.4	97.0	0.4	406
3	62.3-64.5	101.2	1.49	81.8	126.5	0.4	455
4	liquid at RT	100.5	0.382	99.2	239.9	34.35	65.2
5	80.0-82.4	99.8	5.919	75.2	190.2	83.05	49.2
6	57.1-57.7	100.3	0.40	100	27.0	70.2	47.3
7	liquid at RT	100.2	0.52	100	32.7	3.55	194
8	164.1-164.5	101.7	23.6	18.4	167.3	125.0	47.6
9	131.4-131.6	100.4	20.9	23.8	189.6	133.6	43.8
10	109.1-110.3	100.4	16.01	25.1	121.0	132.3	49.2

Each sample was made with DOSS Stamulse surfactant content. Sheets were made from a pulp of freeness number 424 at a grammage of 100g/m^2;
RT* – room temperature;
[a] The Hercules photosize size test (HST) that measures the decrease in reflectance of the opposite side of a sheet of sized paper, which has been covered with 10mL of 1% formic acid dye solution;
[b] CST results are the weight of water retained by a paper sample of a fixed area after 1 minute of pouring 100 mL of distilled water over the sample



Scheme 5: Reaction of ASAs with methanol under dry conditions

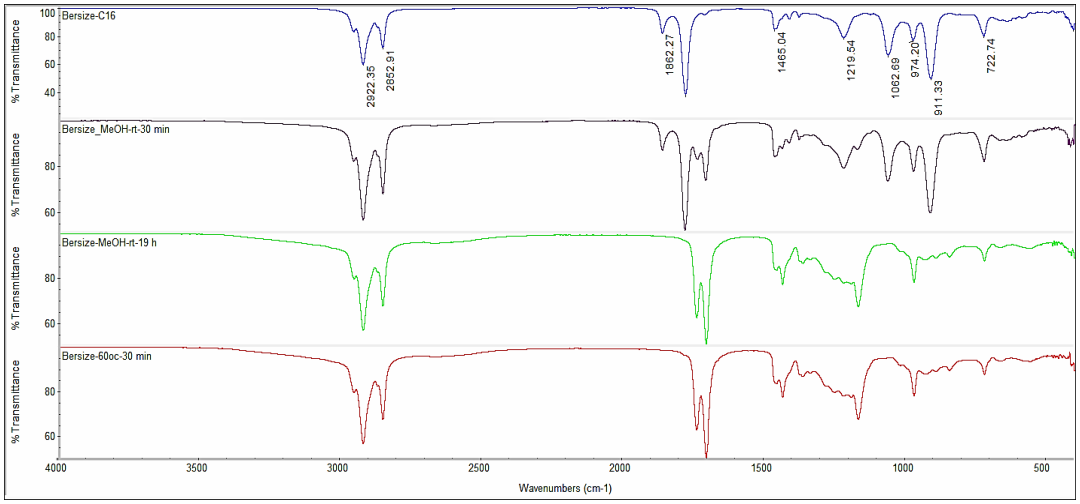


Figure 3: IR spectra illustrating the progression of the reaction between dry methanol and Bersize at room temperature and at 60 °C

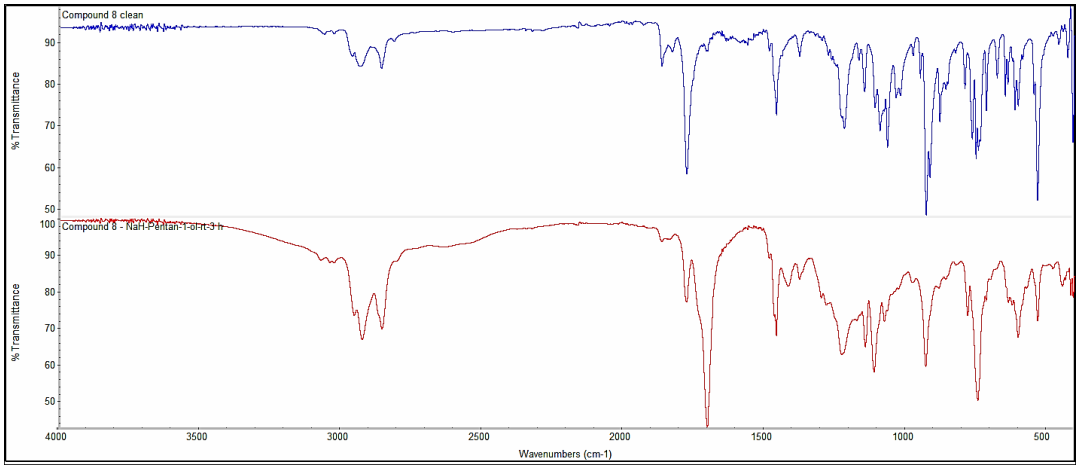


Figure 4: IR spectra of the products obtained by reacting **8** with sodium pentanolate

The CST results reported in Table 1 represent the weight of water retained by a paper sample of a fixed area after 1 minute of pouring 100 mL of distilled water over the sample. Since a single sheet has a large enough surface area to perform multiple HST and CST measurements, these two tests were performed multiple times on the same handsheet.

Evaluation of the reactivity of these compounds toward alcohols used as a substitute for the cellulosic hydroxyl groups

As a control, the reactivity of standard ASA sizing agents (Bersize® 6936 and 7938) toward anhydrous methanol used as reagent and solvent, under argon environment, was investigated (Scheme 5). Each reaction was set up separately, and the reaction mixture was analyzed by IR, after the excess of alcohol was vaporized, and the residue dried in the vacuum-oven for 24 hours.

It appeared that at room temperature, the opening of the succinic anhydride moiety in ASA starts in only 30 minutes at room temperature, as illustrated by Figure 3 (purple spectrum), as compared to the IR spectrum of the starting material (Fig. 3, navy blue spectrum), and completed in 19 hours or less (Fig. 3, green spectrum). When performed at 60 °C, the reaction was completed after only 30 min, as illustrated by Figure 3 (red spectrum). It is important to mention that this temperature is well below that used during the paper sizing process. The reactivity of compounds **1**-**10** toward methanol and pentan-1-ol, used as a substitute for the cellulosic hydroxyl groups, was investigated using similar conditions under which the ASA sizing agent (Bersize®) readily reacted. Surprisingly, any single one of these compounds systematically failed to react, and the starting material was collected each time. In fact, even compounds **8**-**10** that have a succinic

anhydride moiety, the reactive functional group in ASA sizing agents, failed to react even when the mixture was heated at 60 °C for up to 2 hours. As a result, the reactivity of these compounds was further investigated by reacting them with the same alcohols, but this time in the presence of a strong base, such as sodium hydride. The alcohol was first stirred with NaH for about 30 min to create the sodium alkoxide intermediate, before any of the starting material to be evaluated was added to the mixture. The excess of alcohol was then removed by rota-evaporation under a reduced pressure, and the residue dried in the vacuum-oven for 24 hours. The analysis of the residues from these reactions by IR indicate that the reaction started after just 30 min of stirring at room temperature, and the starting material was fully consumed after 24 h as illustrated in Figure 4. Furthermore, under these conditions, all these compounds including maleimide derivatives (**1**-**4**) and maleimide-adducts of anthracene (**5**-**7**), reacted easily, and the reaction was completed within 24 h as indicated by IR analysis of the vacuum oven-dried reaction residues.

RESULTS AND DISCUSSION

A series of maleimide derivatives (**1**-**4**), maleimide Diels-Alder adducts of anthracene (**5**-**7**) and succinic anhydride Diels-Alder adducts of anthracene (**8**-**10**) were evaluated for their sizing properties on paper handsheets, using standard alkenyl succinic anhydride (ASA) sizing agents (C_{16}-ASA – Bersize® 6936 and C_{18}-ASA – Bersize® 7938) as positive controls. Two methods, namely, the Hercules photosize test (HST) and the Cobb size test (CST) were used to evaluate these compounds and the obtained results are summarized in Table 1. It appears that all the tested compounds displayed a weak internal sizing effect nowhere comparable to that of the standard internal sizes Bersize® 6936 and 7938. In fact, even compounds **8**-**10** that possess the exact same succinic anhydride reactive moiety as the standard sizing agents, displayed only a marginal sizing effect in comparison to the positive control. Bersize®6936 and 7938 took about 1125.3 and 1200.0 seconds, respectively, to absorb enough ink to produce the expected reflectance in the HST assay, while in the CST assay, these two sizes absorb about only 31.0 and 18.0 g of water per m² in 1 minute, respectively. The succinic anhydride Diels-Alder adducts of anthracene (**8**-**10**) took only about 125.0, 133.6 and 132.3 seconds, respectively to absorb enough ink to produce the expected reflectance in the HST assay, while taking in 47.6, 43.8 and 49.2 g of water per m² in 1 minute, respectively in the CST assay. As weak as these numbers appear in comparison to that of the standard ASA sizing agents, they represent a significant improvement from the maleimide derivatives that took only 0.4 seconds to absorb enough ink in the HST assay, and absorb up to 475 g of water per m² in 1 minute in the CST assay. Maleimide Diels-Alder adducts of anthracene (**5**-**7**) displayed slightly better sizing effect than the maleimide derivatives, taking 83.05, 70.2 and 3.55 seconds respectively, to absorb enough ink in the HST assay, and adsorb up to 49.2, 47.3 and 194 g of water per m² in 1 minute, respectively in the CST assay.

It is important to mention that all these compounds were evaluated as internal sizing agents, a process in which samples are first emulsified and reacted with a suspension of a paper pulp before it is turned into a handsheet, for the HST and CST assays. As a result, the reactivity of each sample with the paper furnish is critical for its retention at the surface of the cellulosic fibers, and thus decisive for its sizing properties. As such, it is conceivable that the low retention rate of these samples at the surface of the paper furnish is responsible for their poor sizing properties, especially since these compounds displayed very strong hydrophobic properties during the blotter assay. Also known as water-drop-absorption assay, the blotter assay measures the time required for droplets of water to be absorbed by a sheet of paper with the surface coated with the sample to be evaluated. In this assay, the sizing agent is deposited on the surface of the handsheet, and unlike in internal sizing assays, the compound does not have to be retained by the cellulosic fibers to display it's hydrophobic effect. While the significant difference in reactivity between maleimides and succinic anhydrides moieties could explain the lack of sizing effect for compounds **1**-**7**, it was quite surprising why succinic anhydride Diels-Alder adducts of anthracene (**8**-**10**) that have the same reactive moiety as the standard ASA sizing agents, displayed such difference in reactivity towards the paper furnish. Since it is well documented that ASAs achieve their sizing effect by covalently reacting with the hydroxyl groups of the paper fibers,[4-9] one would expect a strong sizing effect from these succinic anhydride Diels-Alder adducts of anthracene since they have a large hydrophobic surface. These data suggest

that having a succinic anhydride moiety in a molecule does not guaranty a good sizing effect, even if the molecule possesses a large hydrophobic area. To be able to rationalize the wide difference in reactivity between these two families of compounds, their reactivity toward simple alcohols used as substitute for the hydroxyl groups of the cellulose fibers was investigated. Cellulose is such a complex molecule that it would have been very difficult to obtain concise and conclusive results for this section of the investigation while using cellulose itself.

As a control, the reactivity of standard ASA sizing agents (Bersize® 6936 and 7938) toward anhydrous methanol used as reagent and solvent, under argon environment was investigated. The fact that these Bersize® ASA products react easily (only within 30 min) with the OH from alcohols at room temperature is in agreement with the formation of a new ester (C-O) bond between the hydroxyl groups of the paper furnish and the succinic anhydride moiety in these ASAs as the potential mechanism of their sizing properties. The reaction was monitored by IR (Fig. 3), and the residue from the reaction fully characterized by NMR to confirm the formation of a new ester bond resulting from the opening of the succinic anhydride ring system as expected. These initial data also provided the baseline for the study of the reactivity of **1**-**10** as potential sizing agents. The expectation from this study was the development of a rationale that can explain why anthracene derivatives with a succinic anhydride moiety similar to that of ASAs failed to produce a level of sizing comparable to that of these standard sizing agents. Surprisingly, while reacted with anhydrous methanol under the exact same conditions as Bersize®6936 and 7938, none of these compounds appeared to be reacting, even after 24 hours, as indicated by the IR spectra of the residues from each of the reactions. This lack of reactivity towards the hydroxyl group in alcohols provides an explanation for the weak sizing effects displayed by these compounds during HST and CST assays. It is important to mention that through the blotter test, all these compounds showed similar or superior hydrophobicity to that of standard ASAs used as positive controls in this study.

Due to the notoriously low reactivity of the amide functional group, compounds **1**-**7** bearing a maleimide as a reactive moiety were expected to be unreactive towards the hydroxyl group in the tested alcohol. However, it was very intriguing that compounds **8**-**10** that have a succinic anhydride reactive moiety did not react under these conditions, especially since anhydrides are known to react very easily with hydroxyl groups either in alcohols or in water. At first, we thought that the steric hindrance around the succinic anhydride moiety in these anthracene derivatives was responsible for this lack of reactivity. However, considering that the succinic anhydride is made of two carbonyl groups, which are sp2 carbons in nature and thus have a trigonal planar geometry, this moiety should have two open sides from which the alcohol could approach and react. Nevertheless, the IR analysis of the reaction mixture indicates that even after 24 hours of reaction with methanol or pentan-1-ol, the succinic anhydride moiety in these compounds was still untouched. In fact, the IR spectrum of the residue from each of these reactions appeared to be identical to that of the starting material, and not even a trace of the product was observed.

A careful analysis of the NMR and single crystal X-ray data obtained from these Diels-Alder adducts of anthracene have indicated that in these molecules, the succinic anhydride or maleimide moiety is bent toward one of the benzene rings of the anthracene. The two planar systems appear to be close enough to create some sort of pi-pi interaction that strongly stabilizes the anhydride moiety. This type of interaction has previously been observed in the NMR spectra and the single crystal X-ray diffraction data of a series of Diels–Alder adducts of anthracene by our research group,[23] and might explain the reduced reactivity of these molecules toward alcohols and water. Figure 5 shows a close up view of the central core of these molecules. Based on these observations, it is possible that pi-pi interactions, rather than steric hindrance are to be blamed for the very strong stability of the succinic anhydride moiety in these anthracene Diels-Alder adducts, resulting in the observed low reactivity.

To investigate the strength of such a stabilization effect, 1-Hexyloxymethyl-dibenzo[e,h]bicyclo[2,2,2]octane(2,3)succinic anhydride (**8**) used as a representative of the succinic anhydride derivative of anthracene, was reacted with pentan-1-ol, in anhydrous THF and in the presence of a very strong base (NaH), as illustrated in Scheme 6.

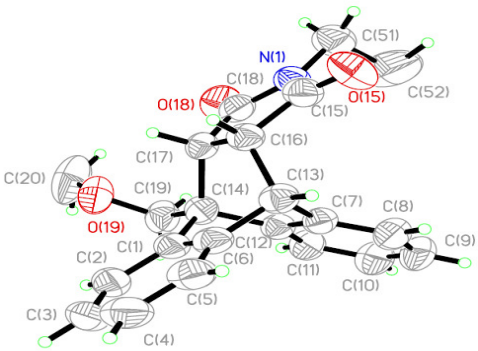
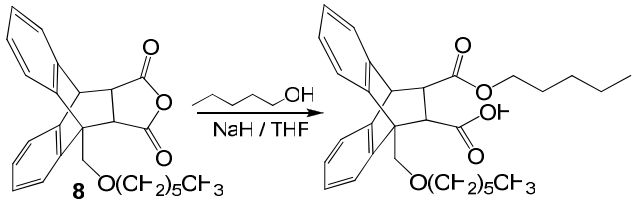
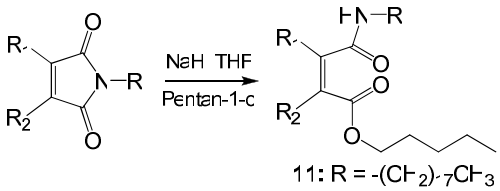


Figure 5: A close up view of the central core of these molecules



Scheme 6: Expected reaction between compound **8** and pentan-1-ol



Scheme 7: Reaction of maleimide derivatives with pentan-1-ol under strong basic conditions

It turned out that under these conditions, the reaction starts only 30 min after the reagents are mixed, and is almost completed after 3 hours as shown by the IR spectrum of the residues obtained from each of these reactions (Fig. 4). This result indicates that alkoxides are reactive enough to disrupt the stabilization effect that prevented these compounds from reacting under previous conditions. In fact, using these latter reaction conditions, we were also able to open some of the maleimide derivatives, namely compounds **3** and **5**. Under these conditions, both compounds were opened at room temperature in less than 24 hours, as illustrated in Scheme 7. In fact, the adduct obtained from opening compound **3**, namely pentyl 4-(octadecylamino)-4-oxobut-2-enoate (**11**) was fully characterized by ^{1}H and ^{13}C-NMR (see the spectra in the supplemental data).

CONCLUSION

A series of maleimide derivatives and Diels-Alder adducts of anthracene have been prepared and evaluated for their sizing properties on a paper handsheet. These compounds displayed good hydrophobicity in the blotter test, but only a weak sizing effect compared to that of standard ASAs. Further investigations have shown that their poor sizing properties on a paper handsheet are the result of their low reactivity toward the hydroxyl groups of the cellulose in the paper furnish. In fact, during this study, standard ASA sizing agents reacted with dry alcohol in a matter of 30 min, while the maleimide derivatives and Diels-Alder adducts of anthracene could not react, even after 24 h, at room temperature and at 60 °C. This lack of reactivity for these succinic anhydride and maleimide adducts of anthracene toward alcohols in the absence of a strong base clearly explains their inadequate sizing effect on the paper handsheet. This work clearly shows that just having a succinic anhydride moiety in a molecule does not guaranty a good sizing effect, even if the molecule possesses a large hydrophobic area. Nevertheless, the fact that these compounds react easily with alcohols in the presence of a strong base could help develop a new sizing protocol to be used for these potential new sizing agents. As hydrolysis during emulsification has been cited as one of the drawbacks of ASAs sizing agents, the advantage of these types of compounds is related to the fact that, unlike ASAs, these new materials will be very resistant to hydrolysis during the emulsification step of the sizing process. However, strong bases, such as NaH, are industrially unpractical, and we are currently

working toward the development of a better method to apply these materials to the paper handsheet. This study also suggests that the reactivity of ASA sizing agents is critical for their sizing effect, and provides an indirect support to the theory of ester bond formation between ASA sizing agents and the hydroxyl groups of the cellulosic fibers.

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