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**Ignacio-de Leon et al.** (43) **Pub. Date: Dec. 8, 2022**

(54) **FILTER MEDIA LAYERS INCLUDING MIXED DIAMETER FINE FIBERS**

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(86) PCT No.: **PCT/US2020/054837**

§ 371 (c)(1),
(2) Date: **Apr. 7, 2022**

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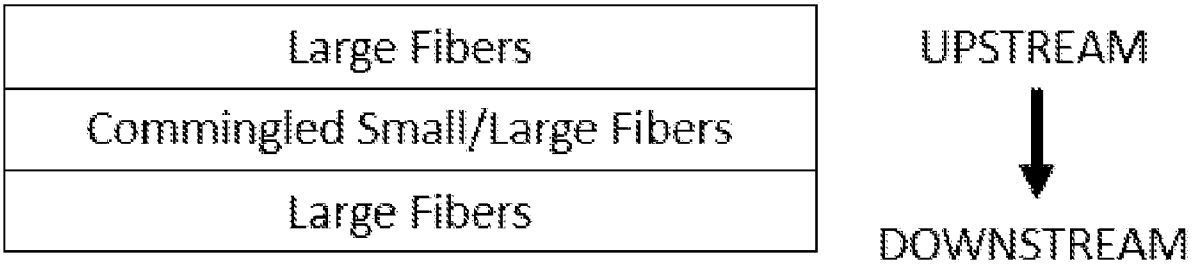
(57) **ABSTRACT**

This disclosure describes a high performing (including, for example, high efficiency and low pressure drop) filter media. The filter media includes a support layer and a layer of fine fibers wherein at least some of the fine fibers in the fine fiber layer having an average diameter at least 3 times the average fiber diameter of a smaller fine fiber in the fine fiber layer. The fine fiber layer may include multiple layers of fine fibers. In some aspects, the smaller fine fiber may be present in the same layer of fine fibers as the larger fine fibers. Additionally or alternatively, the larger fine fibers may be present in a first layer of fine fibers and the smaller fine fibers may be present in a second layer of fine fibers.



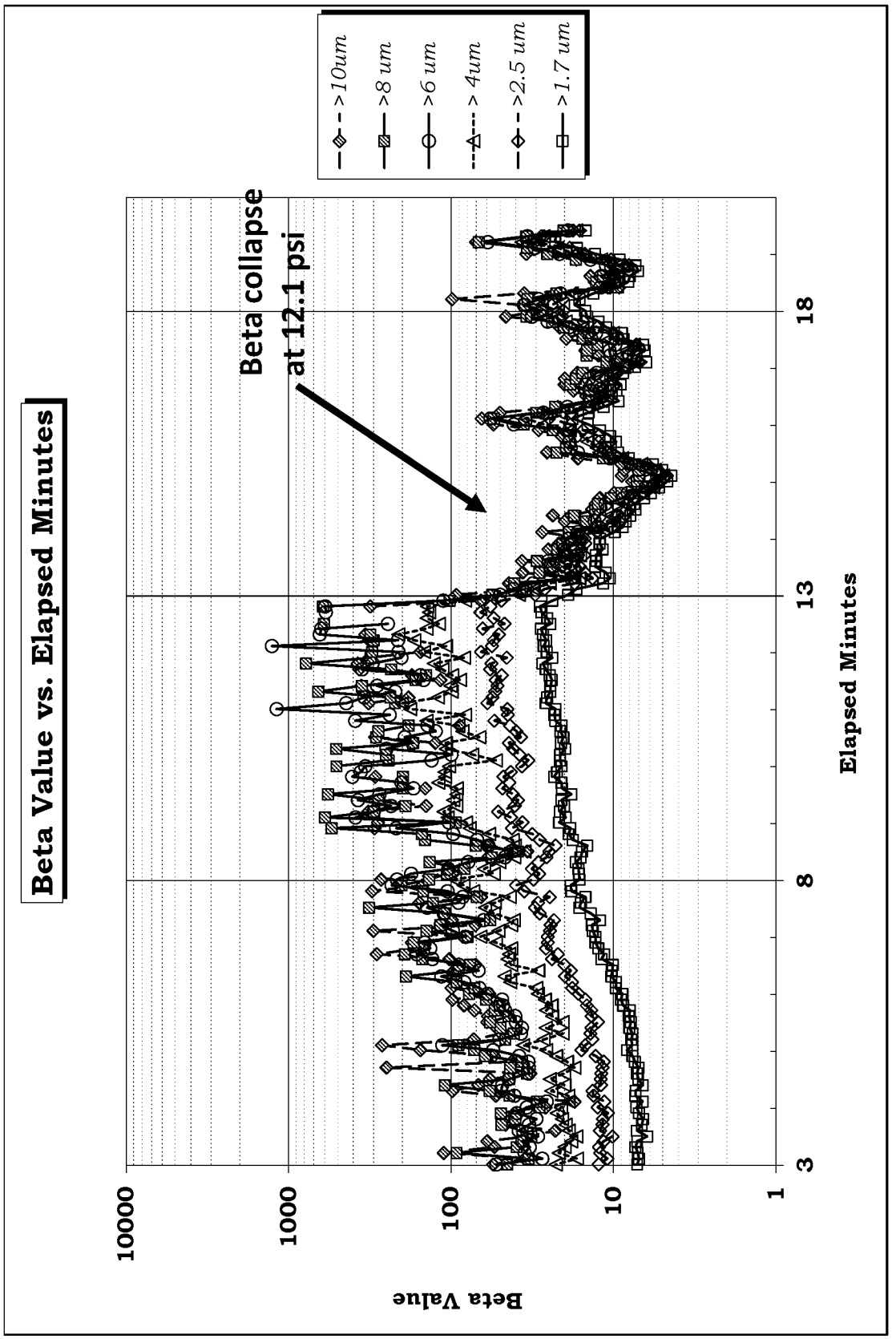
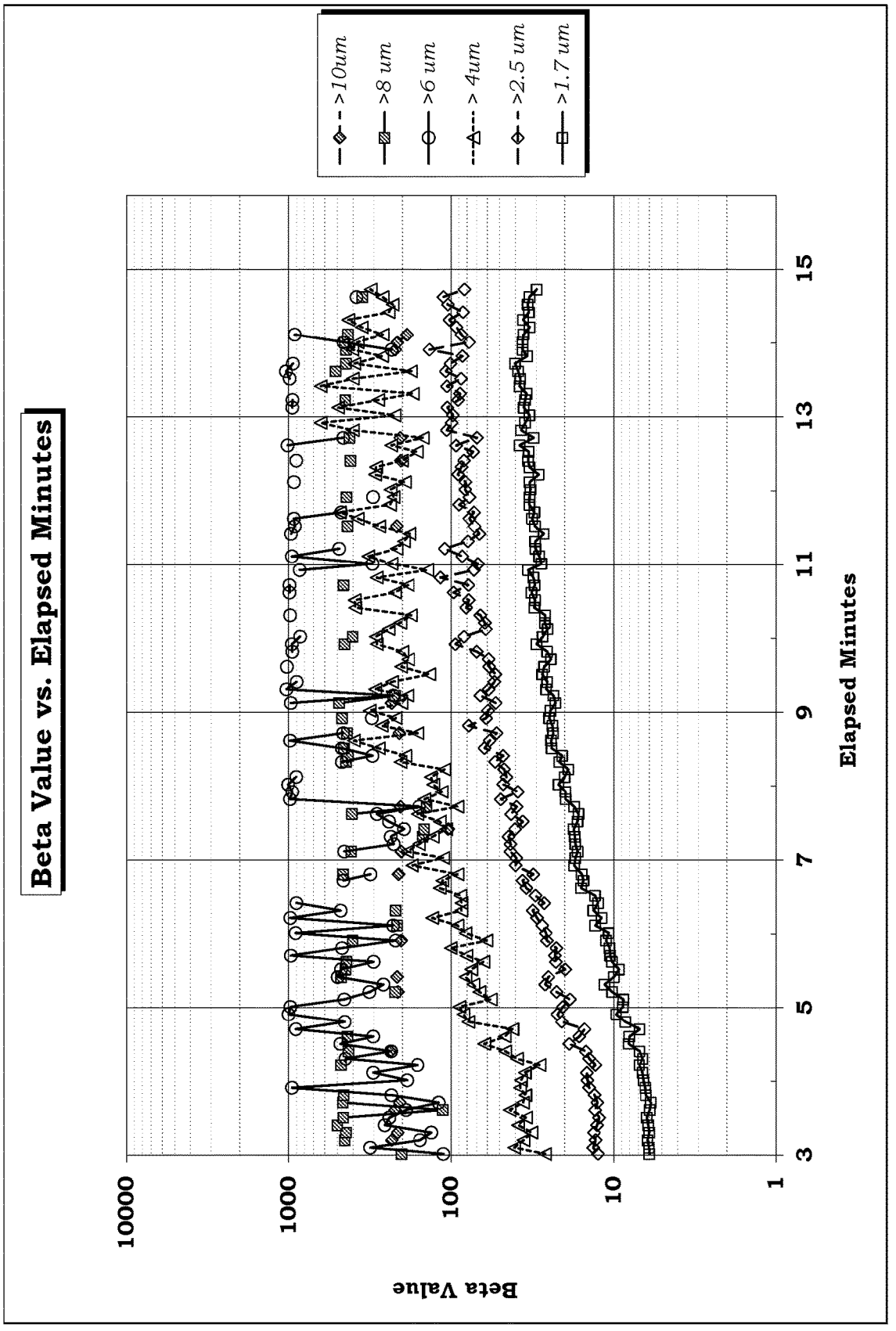

Beta Value vs. Elapsed Minutes
Beta collapse at 12.1 psi
>10um
>8 um
>6 um
>4um
>2.5 um
>1.7 um
Beta Value
10000
1000
100
10
1
Elapsed Minutes
3
8
13
18

FIG. 1A


Beta Value vs. Elapsed Minutes
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>8 um
>6 um
> 4um
>2.5 um
>1.7 um
10000
1000
100
10
1
Beta Value
3
5
7
9
11
13
15
Elapsed Minutes

FIG. 1C

FIG. 1B

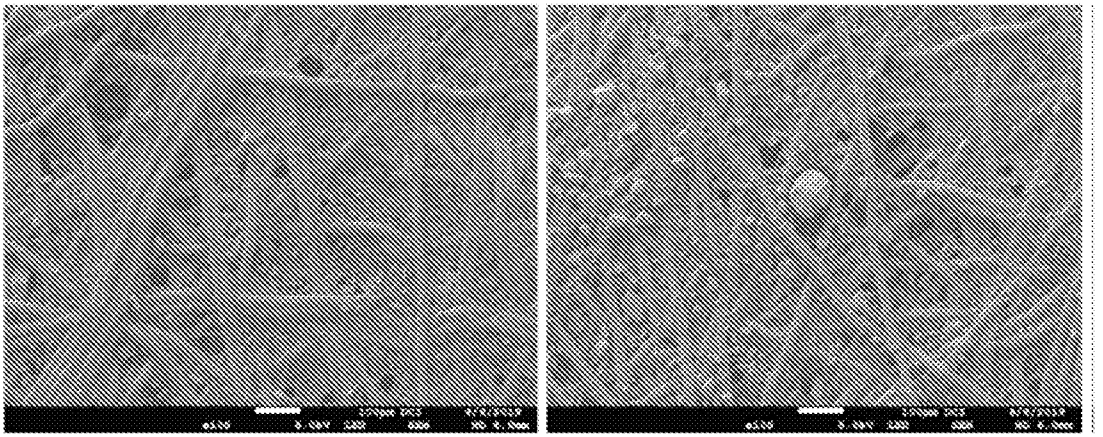


FIG. 1D

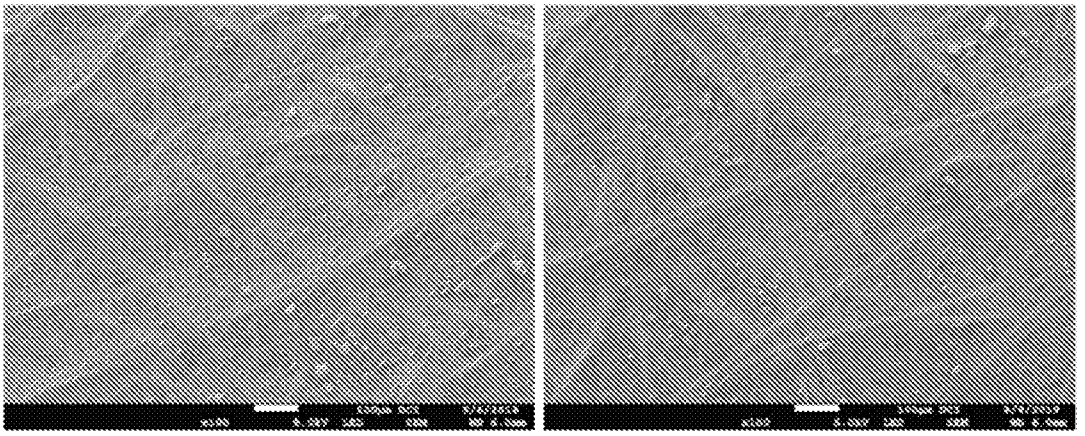
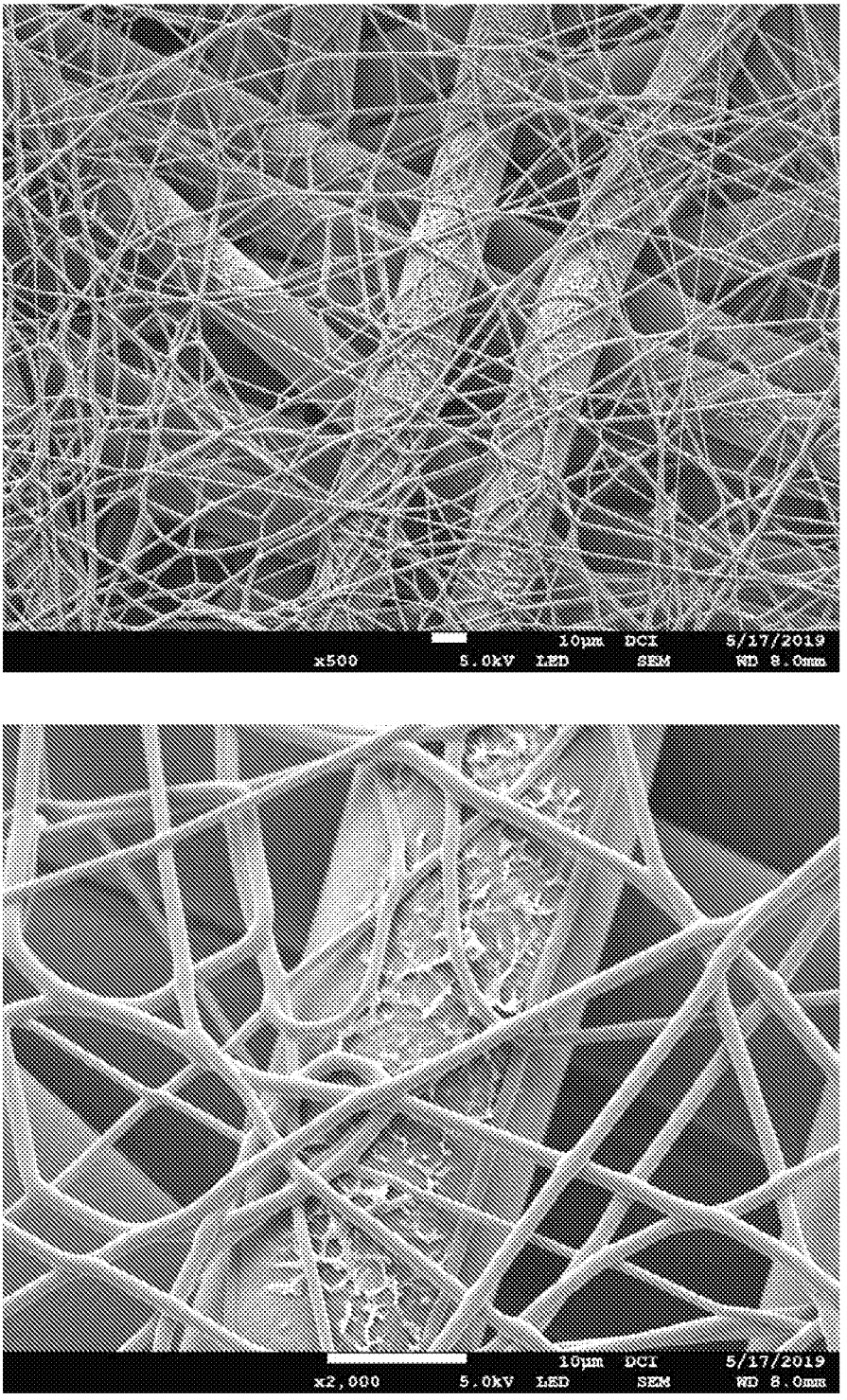


FIG. 1E


10μm DCI 5/17/2019
x500 5.0kV LED SEM WD 8.0mm
10μm DCI 5/17/2019
x2,000 5.0kV LED SEM WD 8.0mm

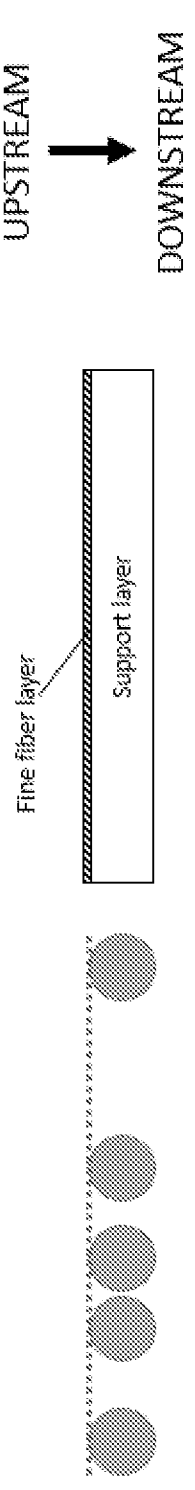

UPSTREAM
DOWNSTREAM
Fine fiber layer
Support layer

FIG. 1F

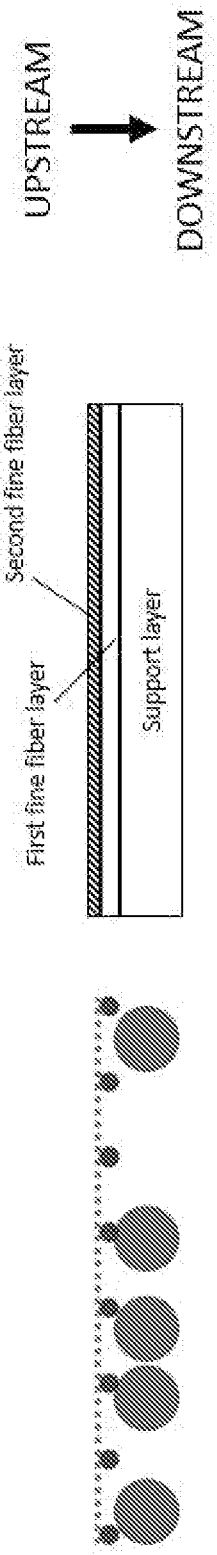

UPSTREAM
DOWNSTREAM
Second fine fiber layer
First fine fiber layer
Support layer

FIG. 1G

FIG. 1H

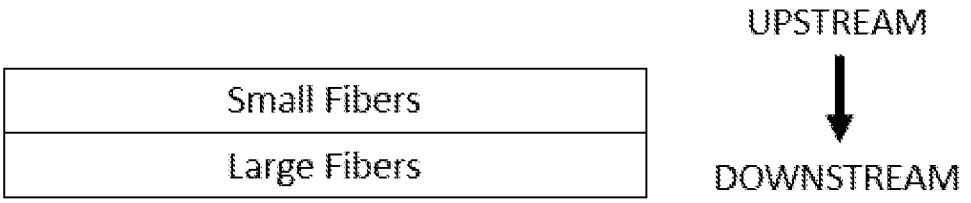



FIG. 1I

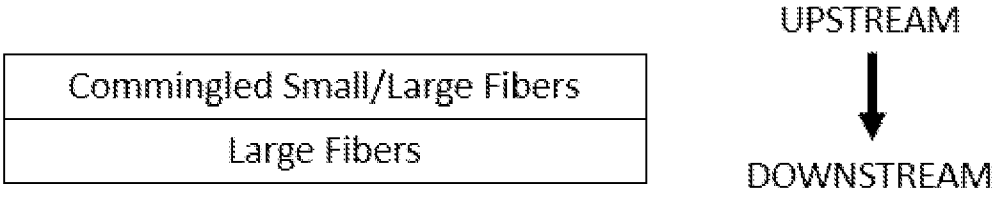



FIG. 1J

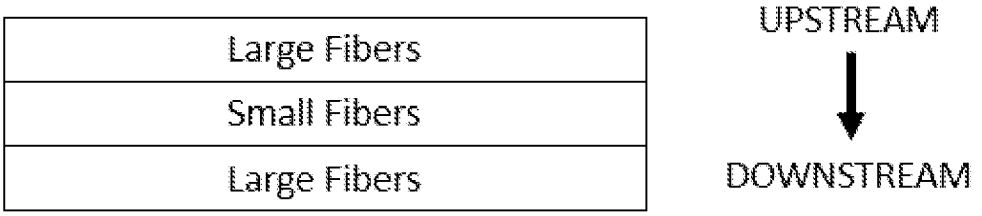



FIG. 1K

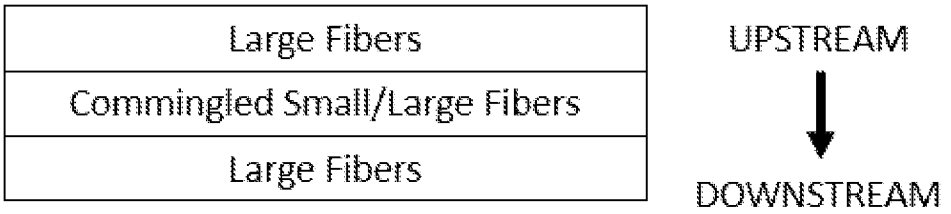


FIG. 1L

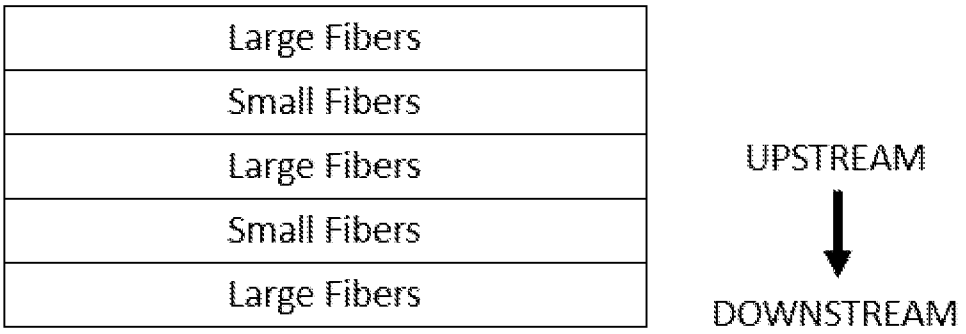
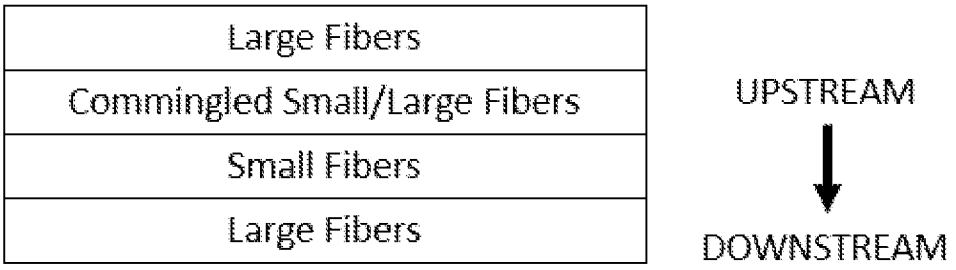

Large Fibers
Small Fibers
Large Fibers
Small Fibers
Large Fibers
UPSTREAM
DOWNSTREAM

FIG. 1M


Large Fibers
Commingled Small/Large Fibers
Small Fibers
Large Fibers
UPSTREAM
DOWNSTREAM

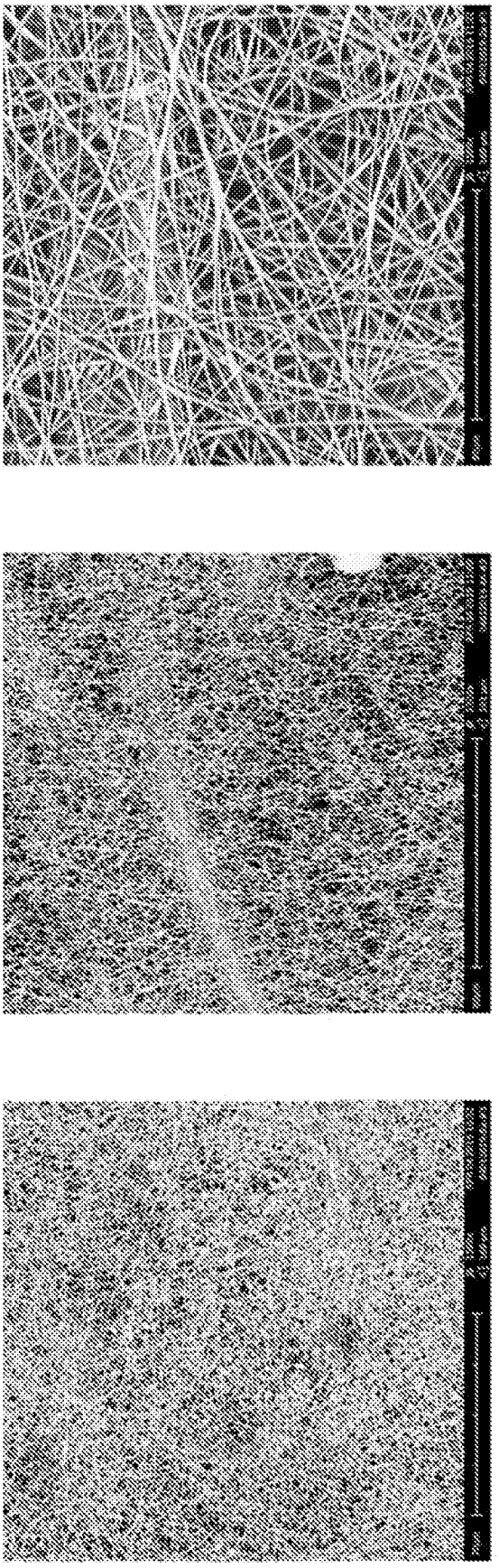


FIG. 2A

FIG. 2B

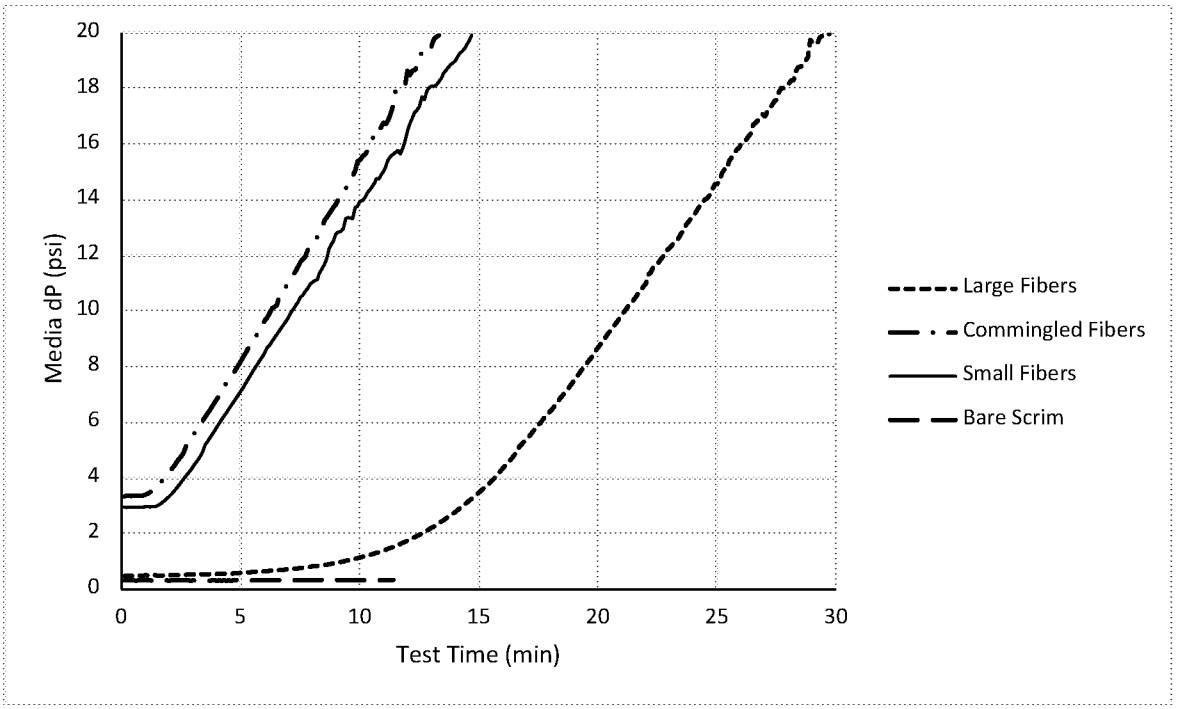
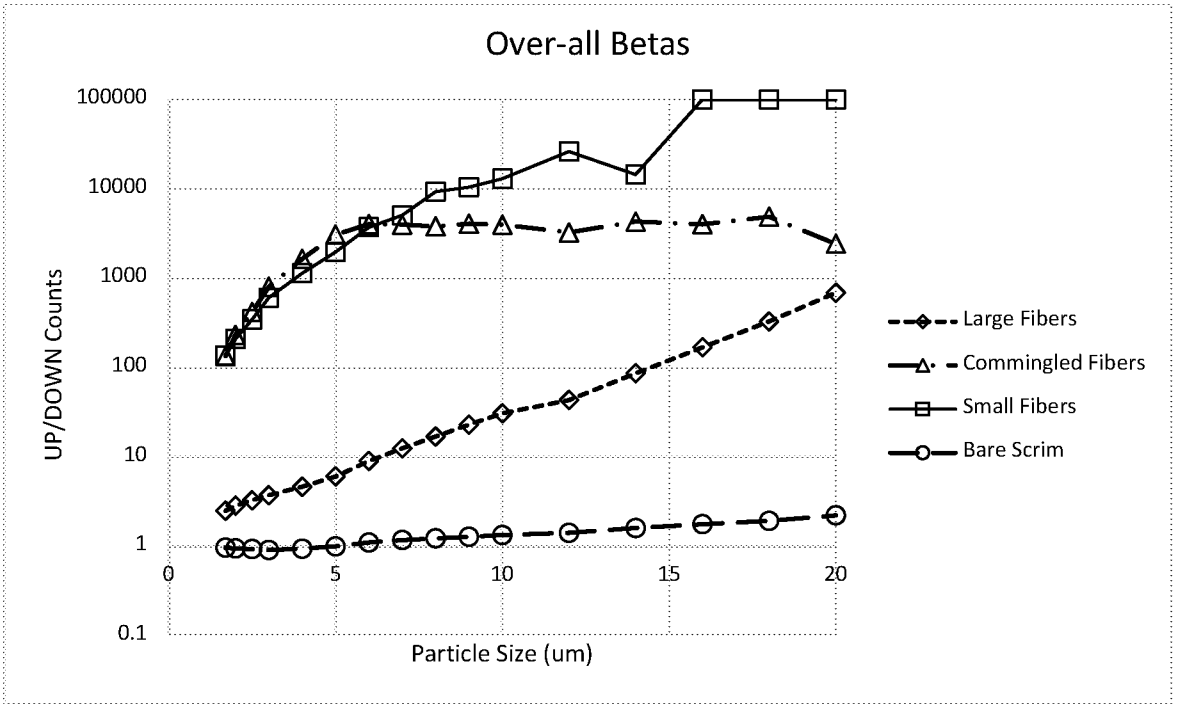

Media dP (psi)
Test Time (min)
Large Fibers
Commingled Fibers
Small Fibers
Bare Scrim

FIG. 2C


Over-all Betas
UP/DOWN Counts
Particle Size (um)
Large Fibers
Commingled Fibers
Small Fibers
Bare Scrim

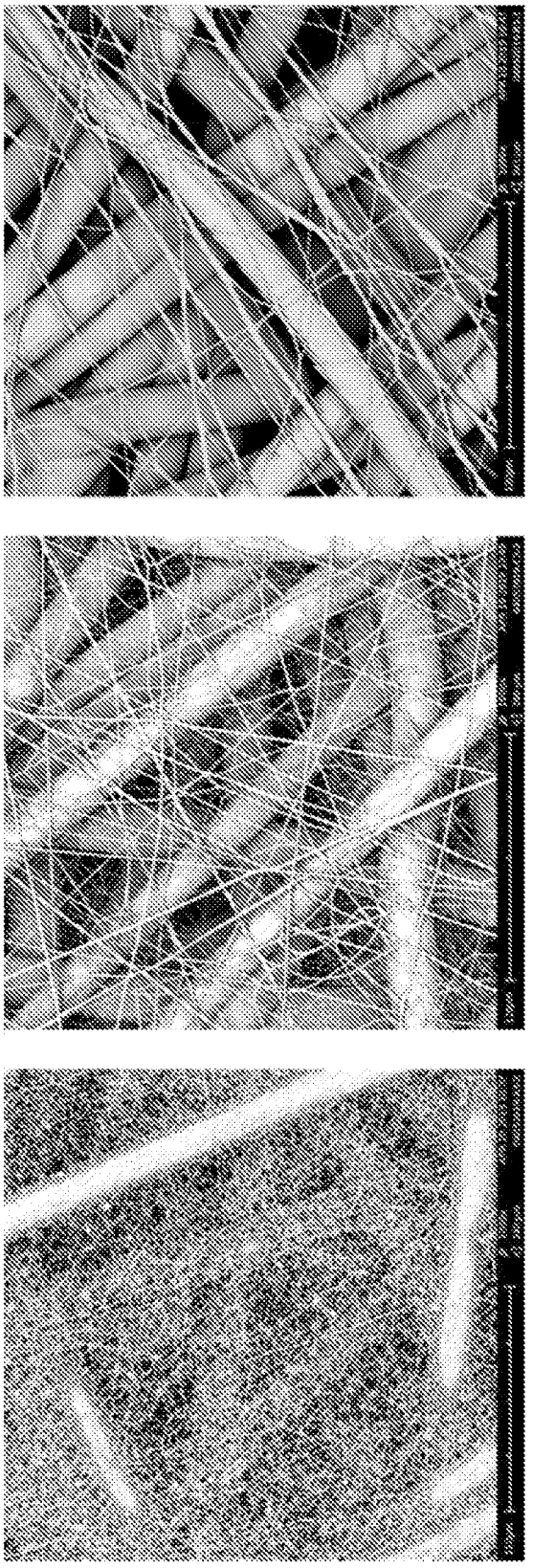


FIG. 3A

FIG. 3B

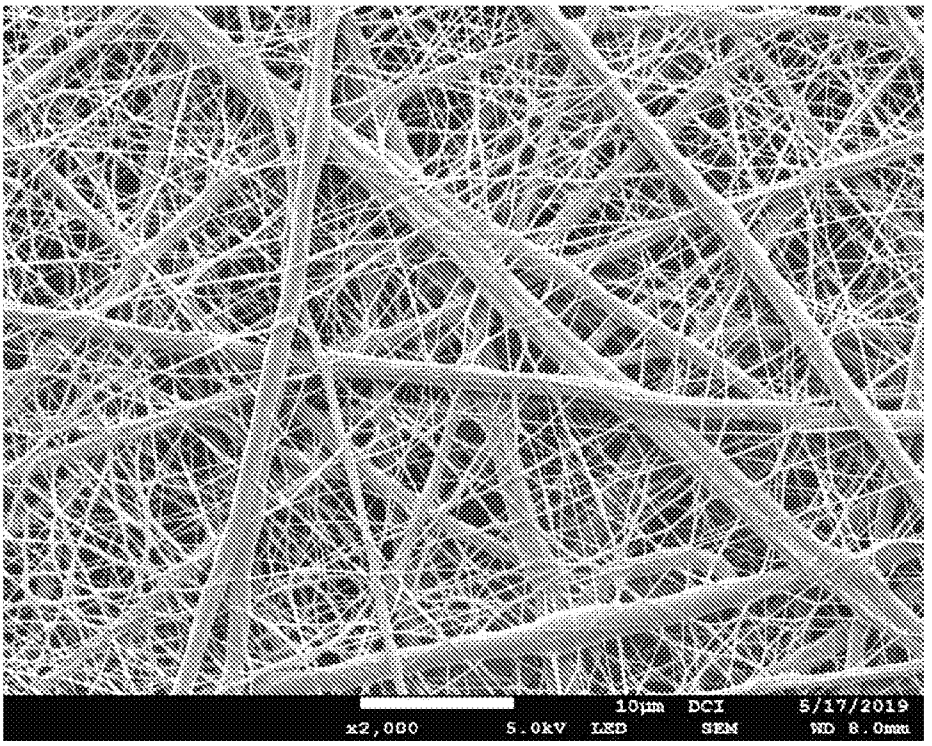

10μm DCI 5/17/2019
x2,000 5.0kV LED SEM WD 8.0mm

FIG. 3C

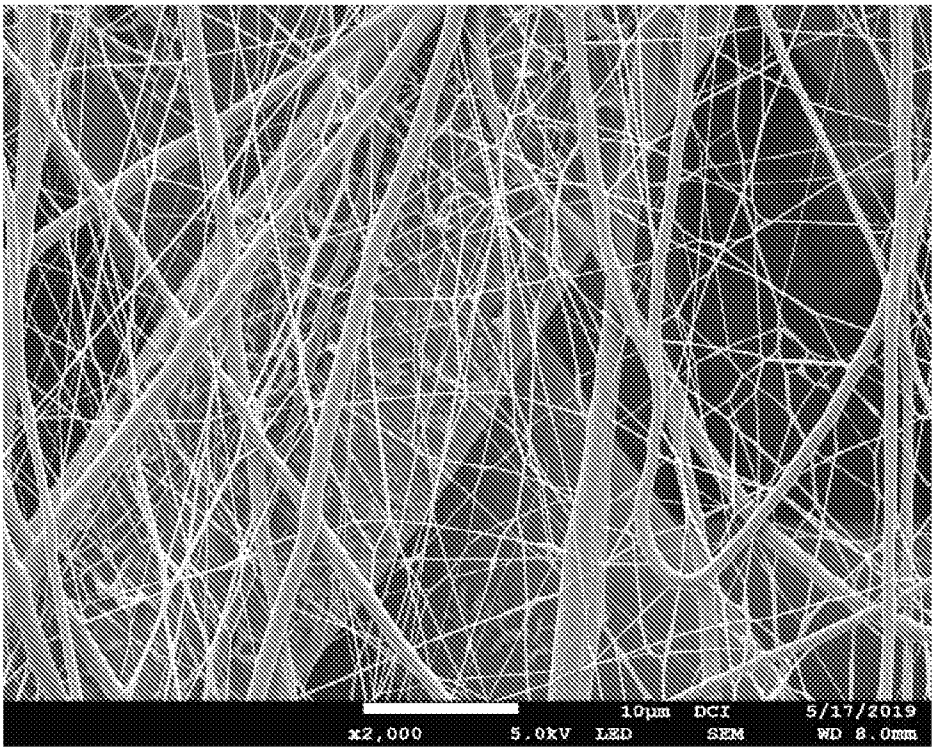

10μm DCI 5/17/2019
x2,000 5.0kV LED SEM WD 8.0mm

FIG. 3D

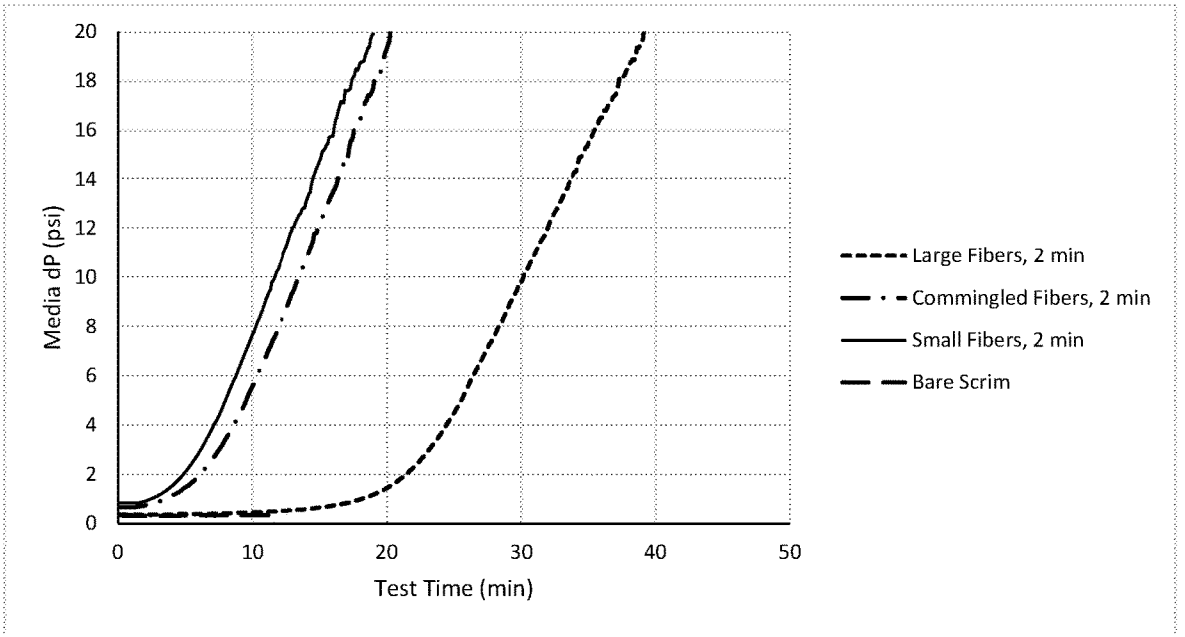

Media dP (psi)
0
2
4
6
8
10
12
14
16
18
20
0
10
20
30
40
50
Test Time (min)
Large Fibers, 2 min
Commingled Fibers, 2 min
Small Fibers, 2 min
Bare Scrim

FIG. 3E

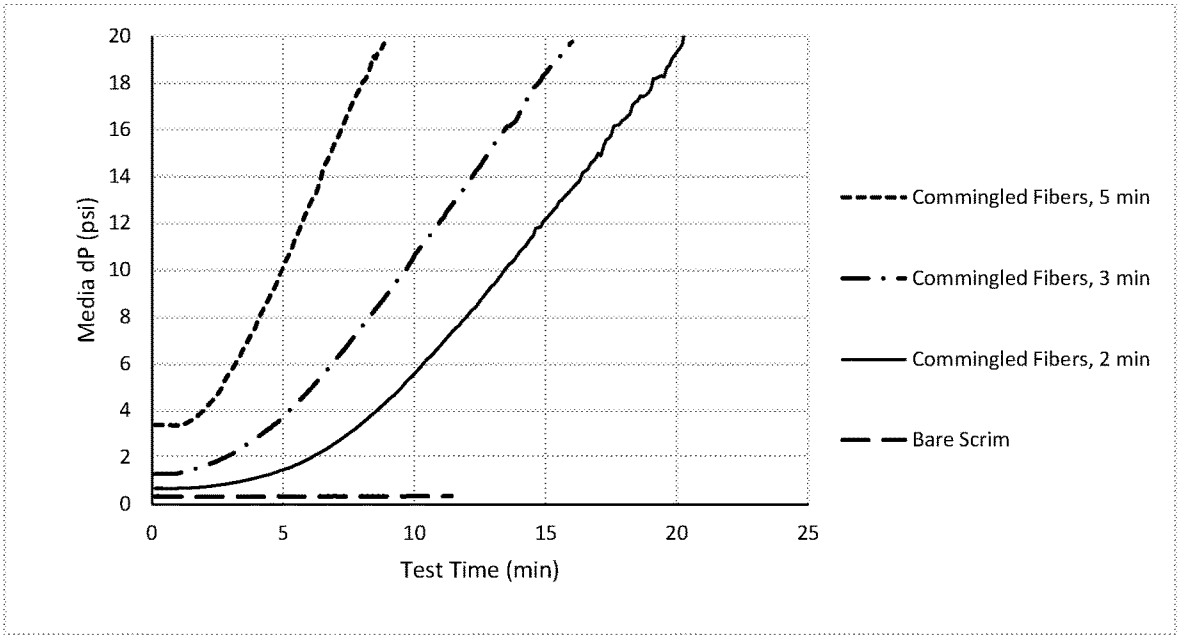

Media dP (psi)
0
2
4
6
8
10
12
14
16
18
20
0
5
10
15
20
25
Test Time (min)
Commingled Fibers, 5 min
Commingled Fibers, 3 min
Commingled Fibers, 2 min
Bare Scrim

FIG. 3F

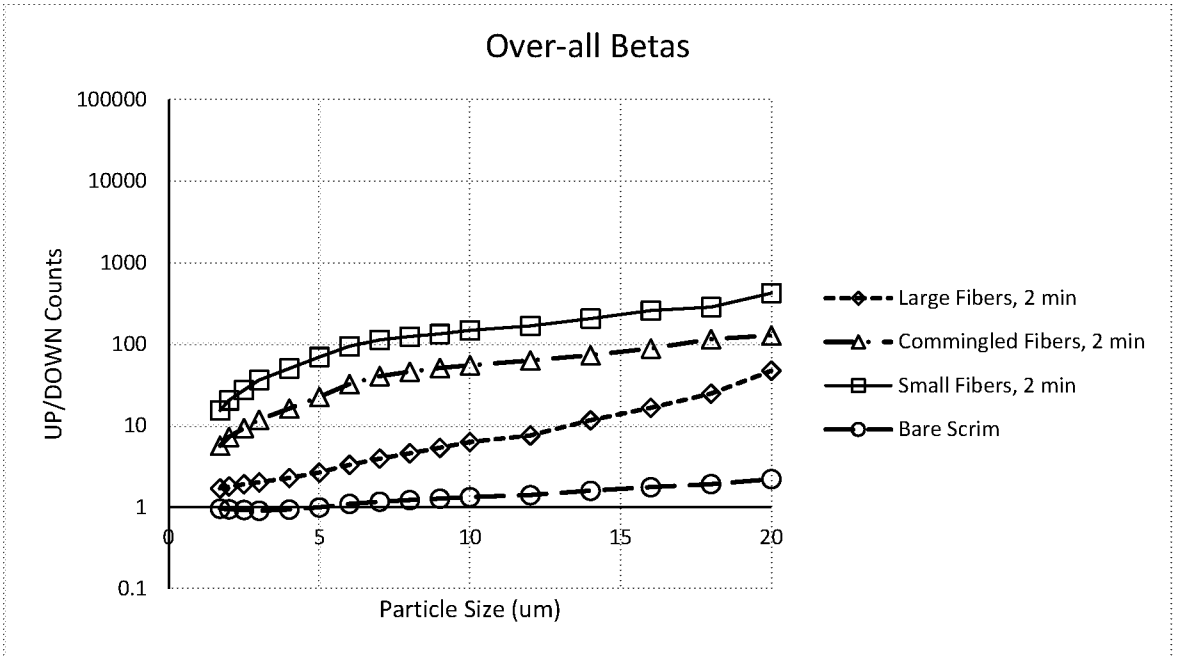

Over-all Betas
UP/DOWN Counts
100000
10000
1000
100
10
1
0.1
0
5
10
15
20
Particle Size (um)
Large Fibers, 2 min
Commingled Fibers, 2 min
Small Fibers, 2 min
Bare Scrim

FIG. 3G

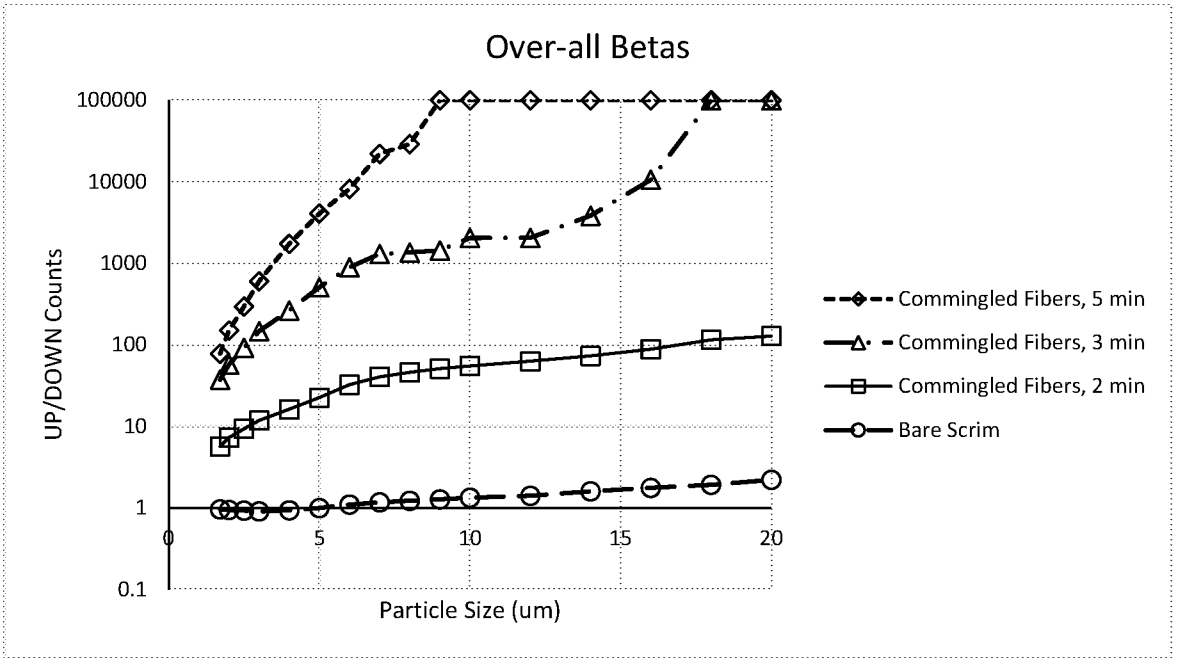
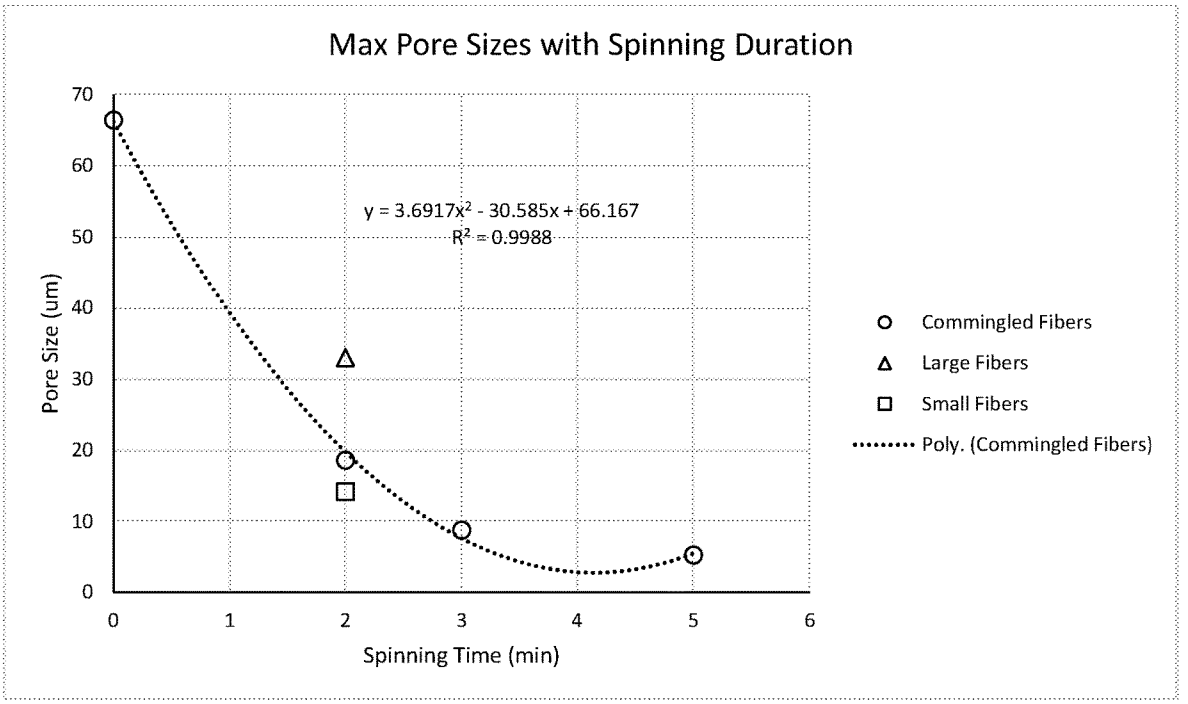

Over-all Betas
UP/DOWN Counts
100000
10000
1000
100
10
1
0.1
0
5
10
15
20
Particle Size (um)
Commingled Fibers, 5 min
Commingled Fibers, 3 min
Commingled Fibers, 2 min
Bare Scrim

FIG. 3H


Max Pore Sizes with Spinning Duration
y = 3.6917x² - 30.585x + 66.167
R² = 0.9988
Pore Size (um)
Spinning Time (min)
Commingled Fibers
Large Fibers
Small Fibers
Poly. (Commingled Fibers)

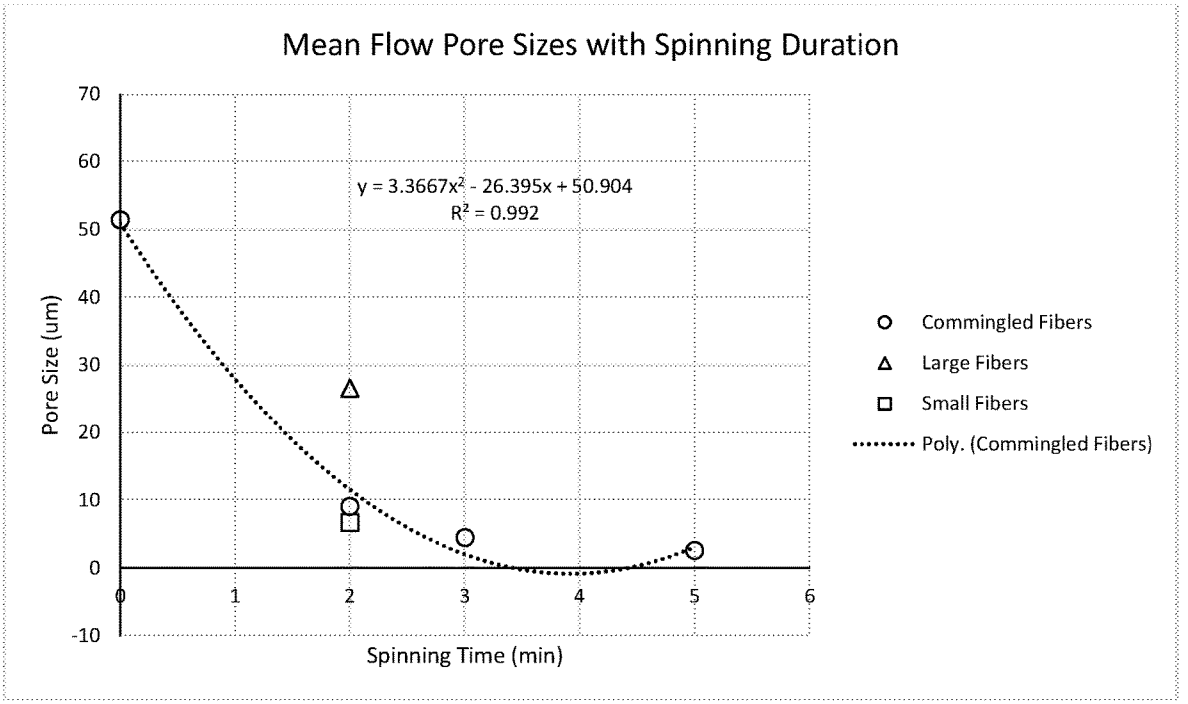
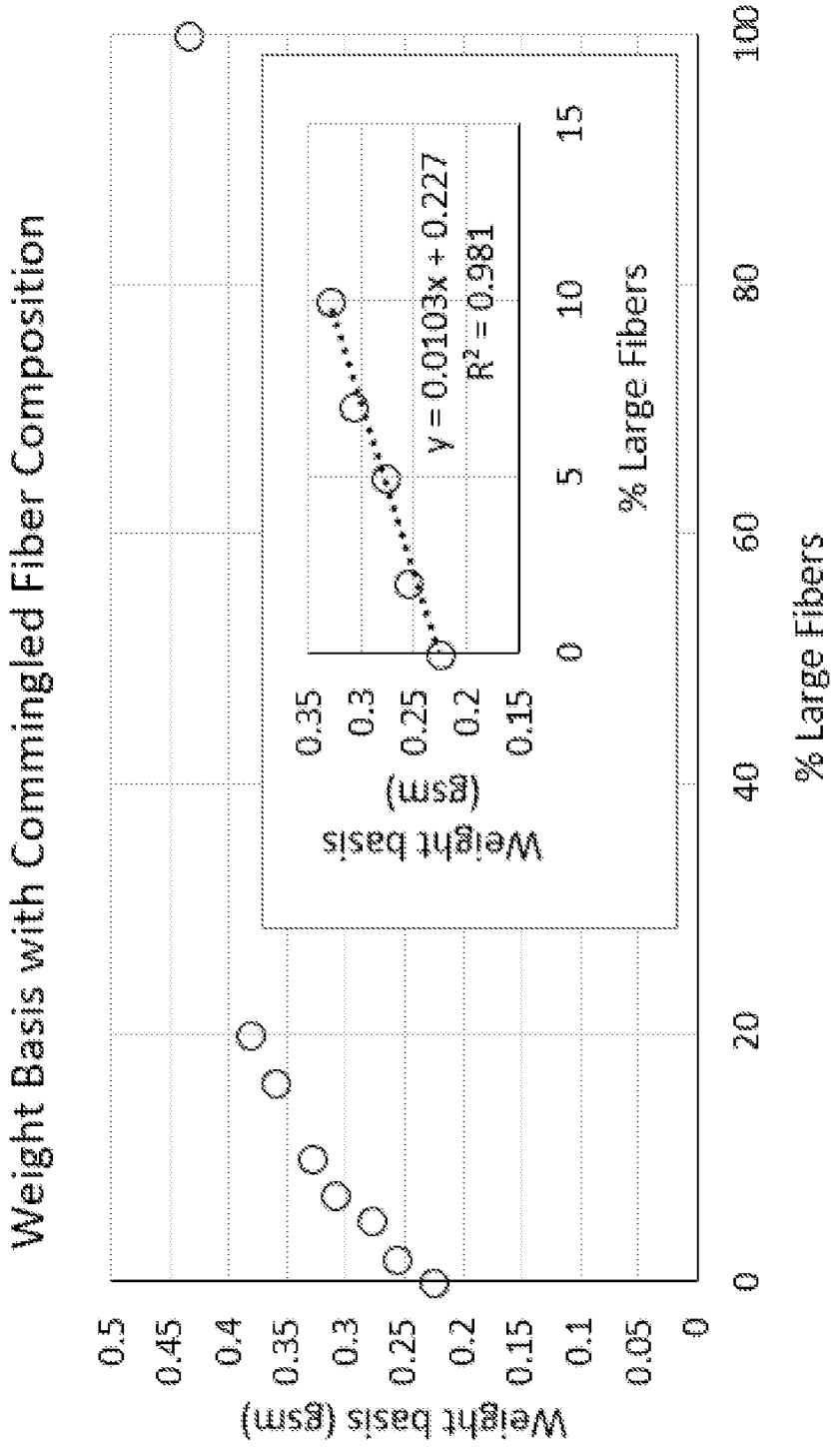

Mean Flow Pore Sizes with Spinning Duration
y = 3.3667x² - 26.395x + 50.904
R² = 0.992
Pore Size (um)
Spinning Time (min)
Commingled Fibers
Large Fibers
Small Fibers
Poly. (Commingled Fibers)

FIG. 4


Weight Basis with Commingled Fiber Composition
Weight basis (gsm)
% Large Fibers
0.5
0.45
0.4
0.35
0.3
0.25
0.2
0.15
0.1
0.05
0
0
20
40
60
80
100
Weight basis (gsm)
0.35
0.3
0.25
0.2
0.15
y = 0.0103x + 0.227
R² = 0.981
0
5
10
15
% Large Fibers

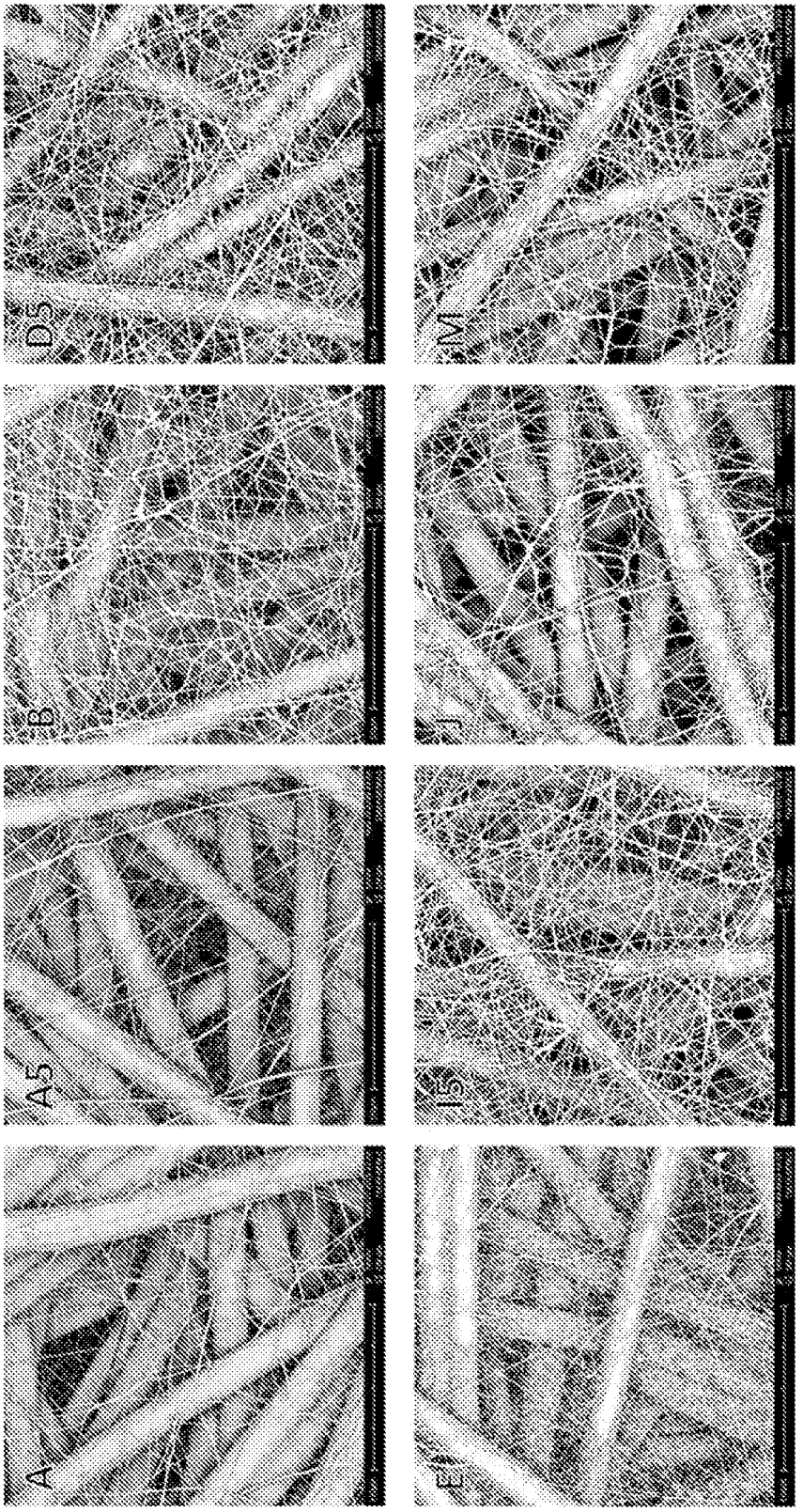



FIG. 5A

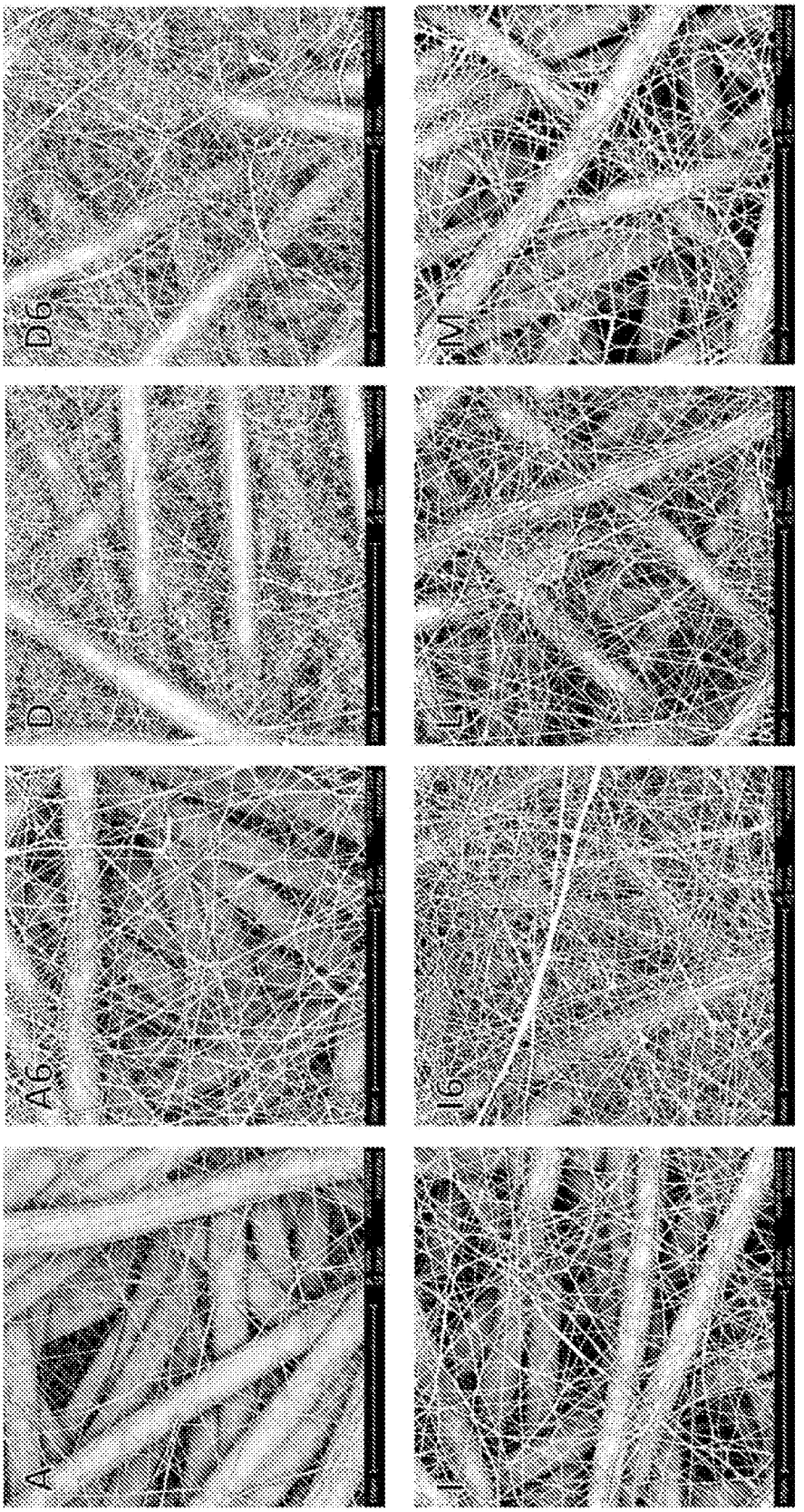
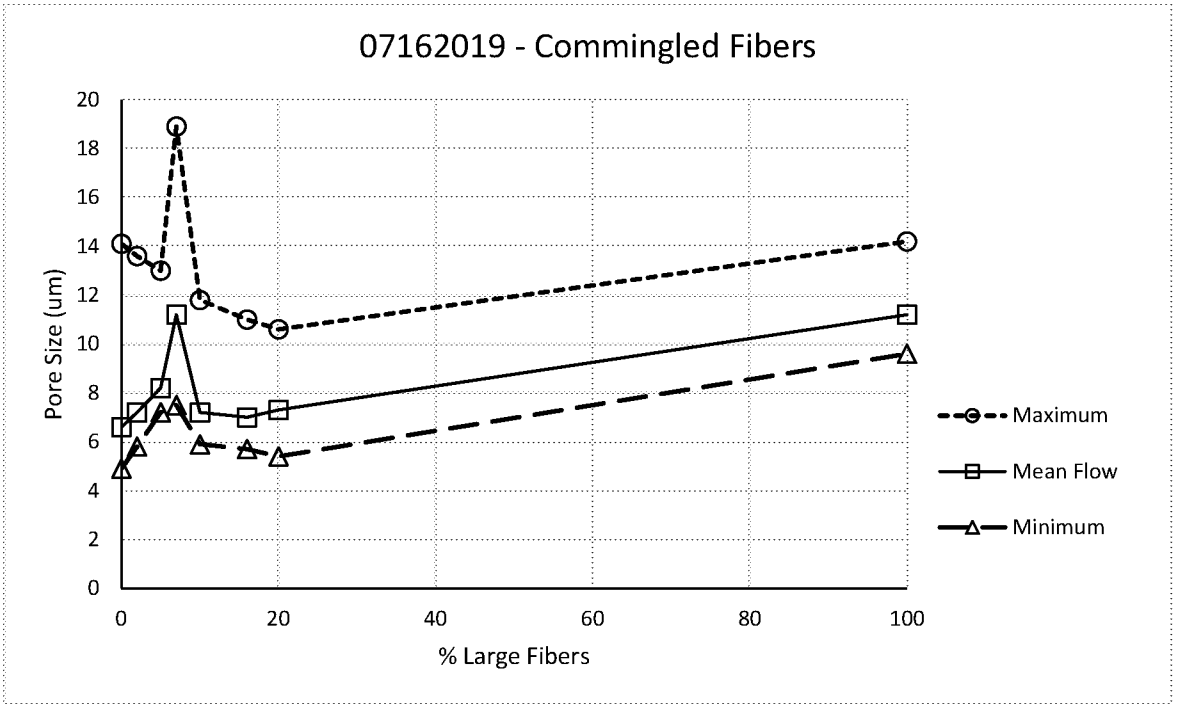



FIG. 5B

FIG. 5C


07162019 - Commingled Fibers
Pore Size (um)
0
2
4
6
8
10
12
14
16
18
20
0
20
40
60
80
100
% Large Fibers
Maximum
Mean Flow
Minimum

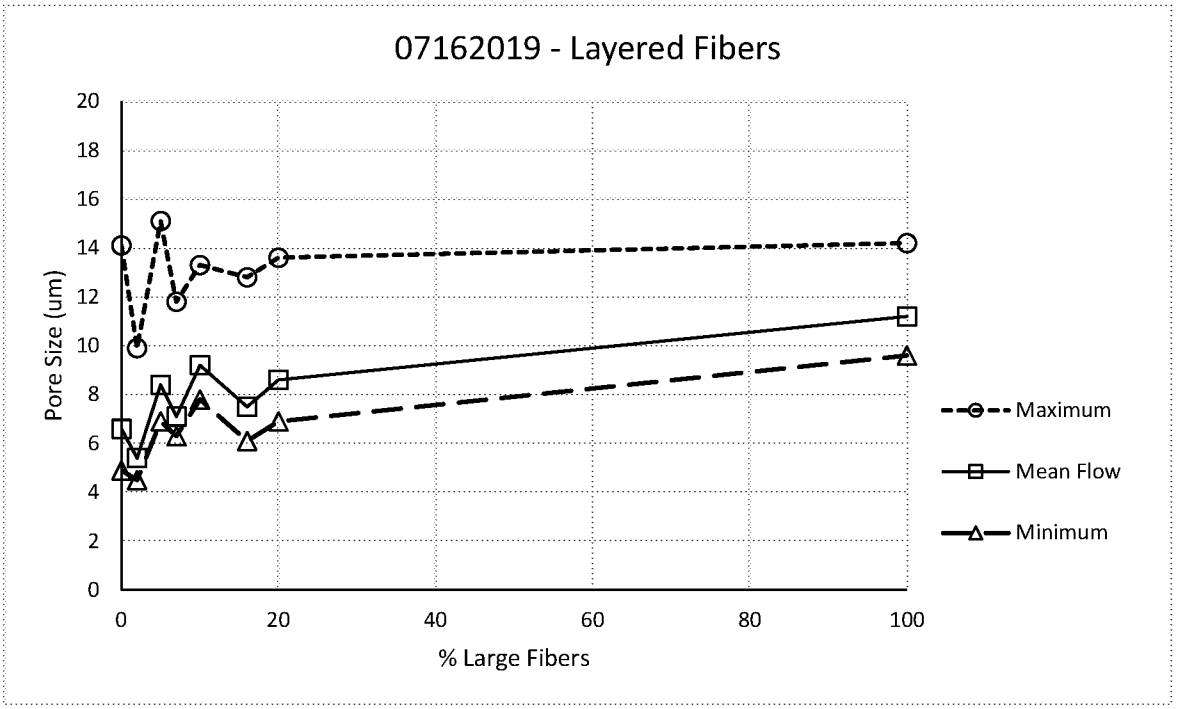
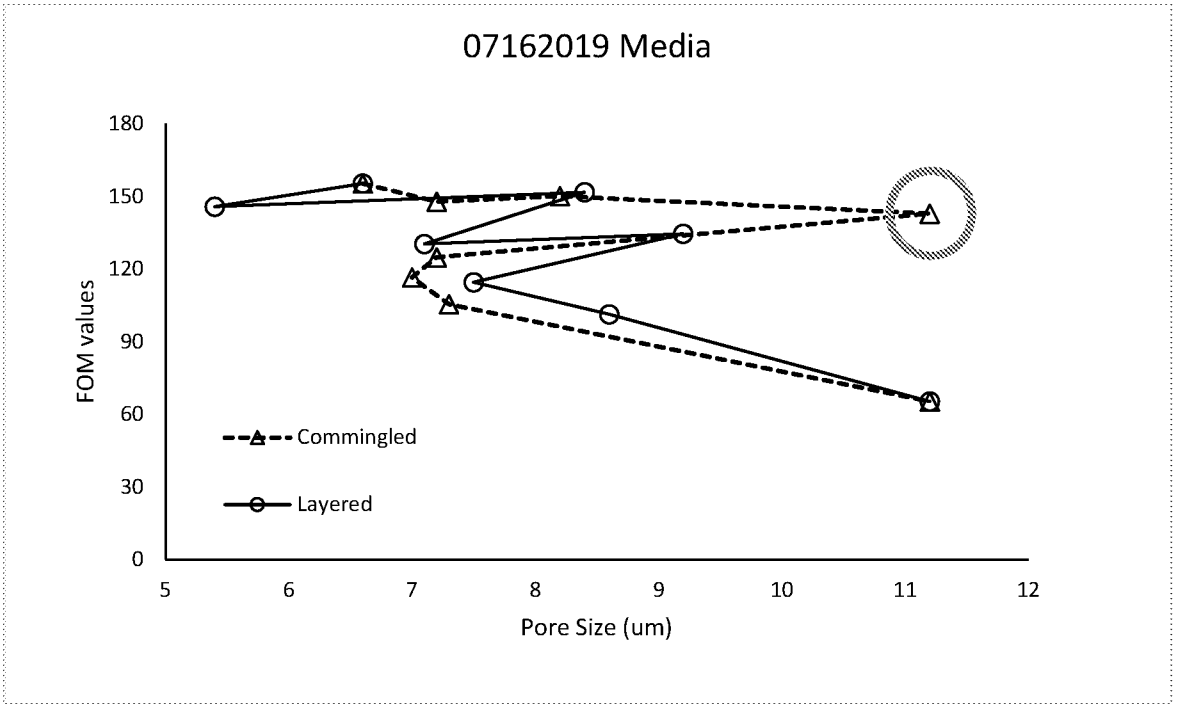
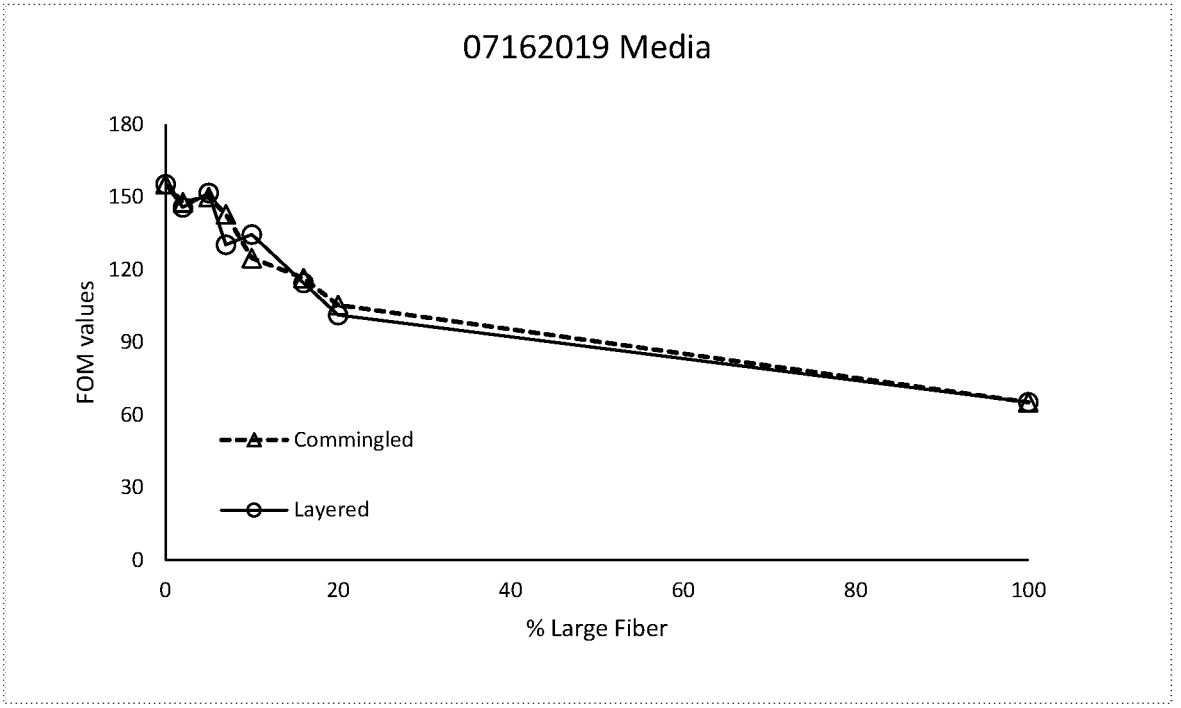

07162019 - Layered Fibers
Pore Size (um)
0
2
4
6
8
10
12
14
16
18
20
0
20
40
60
80
100
% Large Fibers
Maximum
Mean Flow
Minimum

FIG. 5D


07162019 Media
180
150
120
90
60
30
0
FOM values
Commingled
Layered
5
6
7
8
9
10
11
12
Pore Size (um)


07162019 Media
180
150
120
90
60
30
0
FOM values
Commingled
Layered
0
20
40
60
80
100
% Large Fiber

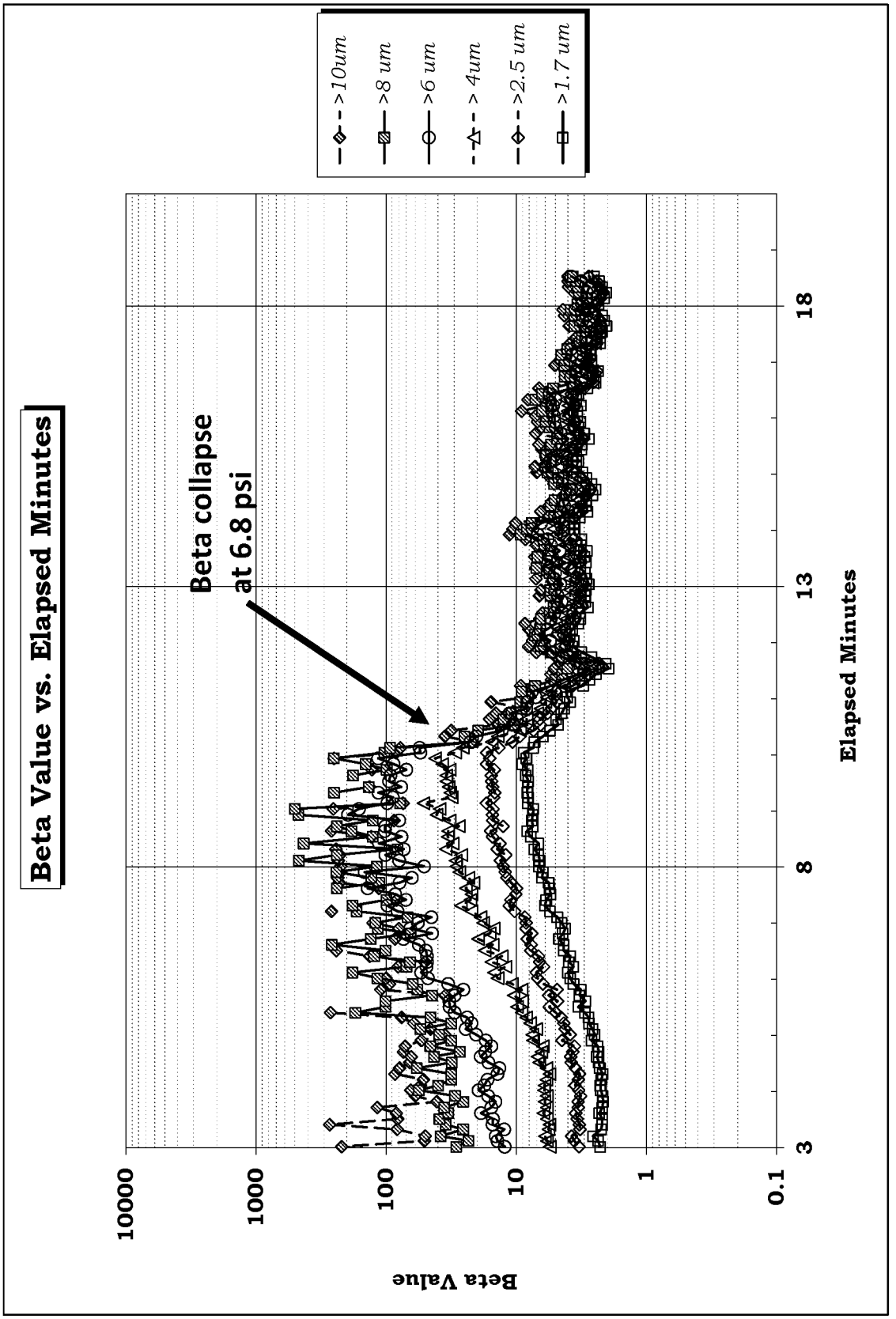

Beta Value vs. Elapsed Minutes
Beta collapse at 6.8 psi
>10um
>8 um
>6 um
> 4um
>2.5 um
>1.7 um
Beta Value
10000
1000
100
10
1
0.1
3
8
13
18
Elapsed Minutes

FIG. 5E

FIG. 5F

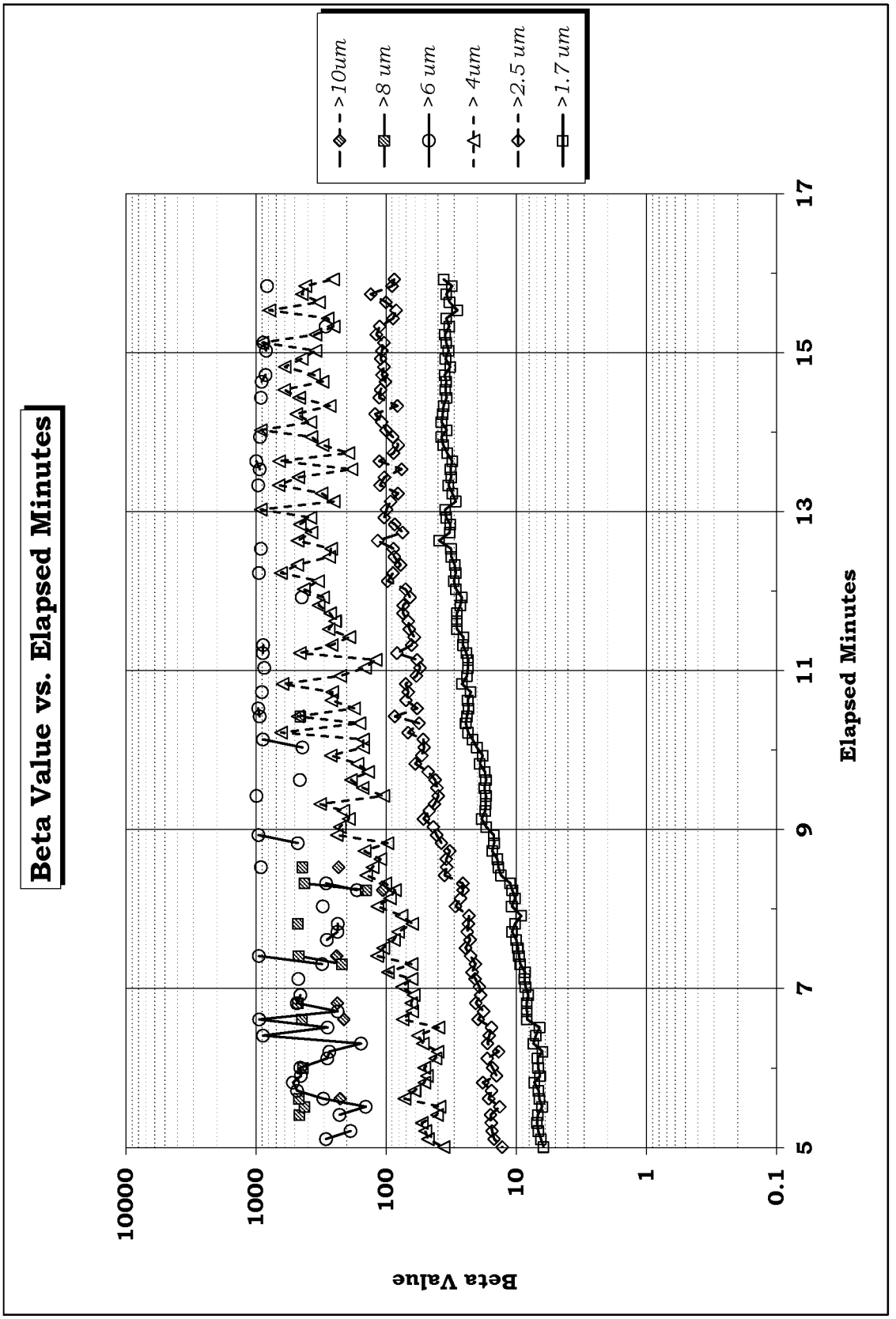
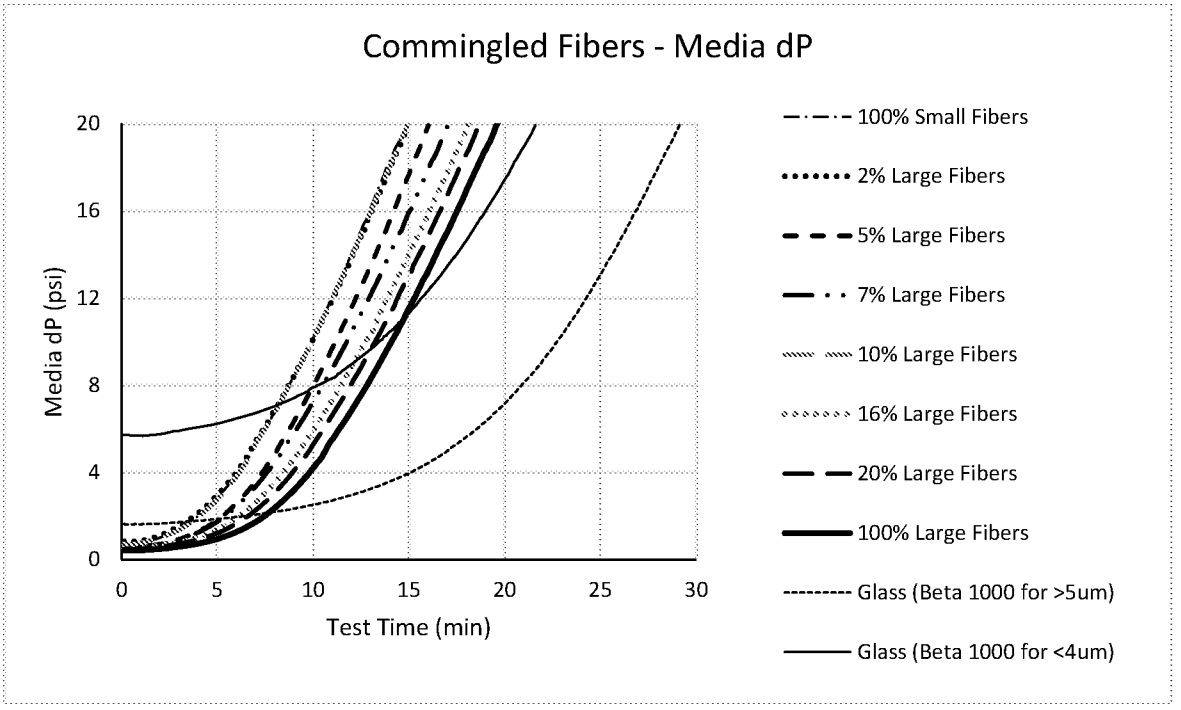

Beta Value vs. Elapsed Minutes
>10um
>8 um
>6 um
> 4um
>2.5 um
>1.7 um
Beta Value
10000
1000
100
10
1
0.1
5
7
9
11
13
15
17
Elapsed Minutes

FIG. 5G


Commingled Fibers - Media dP
Media dP (psi)
Test Time (min)
0
4
8
12
16
20
0
5
10
15
20
25
30
100% Small Fibers
2% Large Fibers
5% Large Fibers
7% Large Fibers
10% Large Fibers
16% Large Fibers
20% Large Fibers
100% Large Fibers
Glass (Beta 1000 for >5um)
Glass (Beta 1000 for <4um)

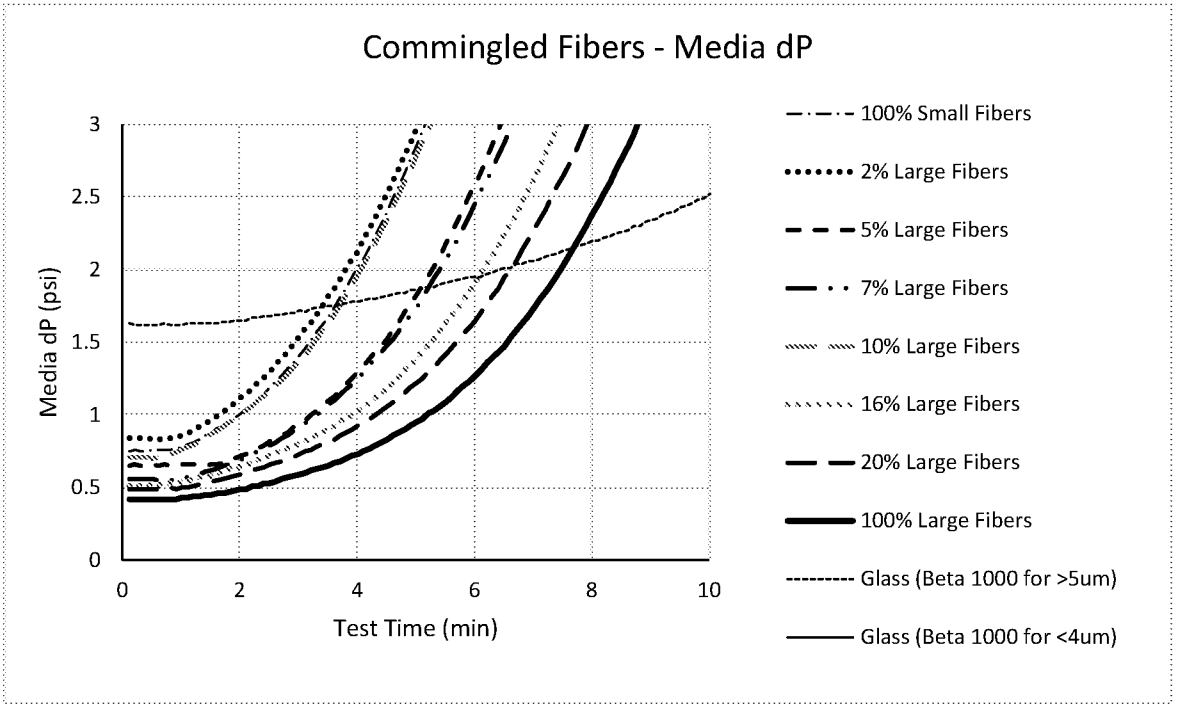
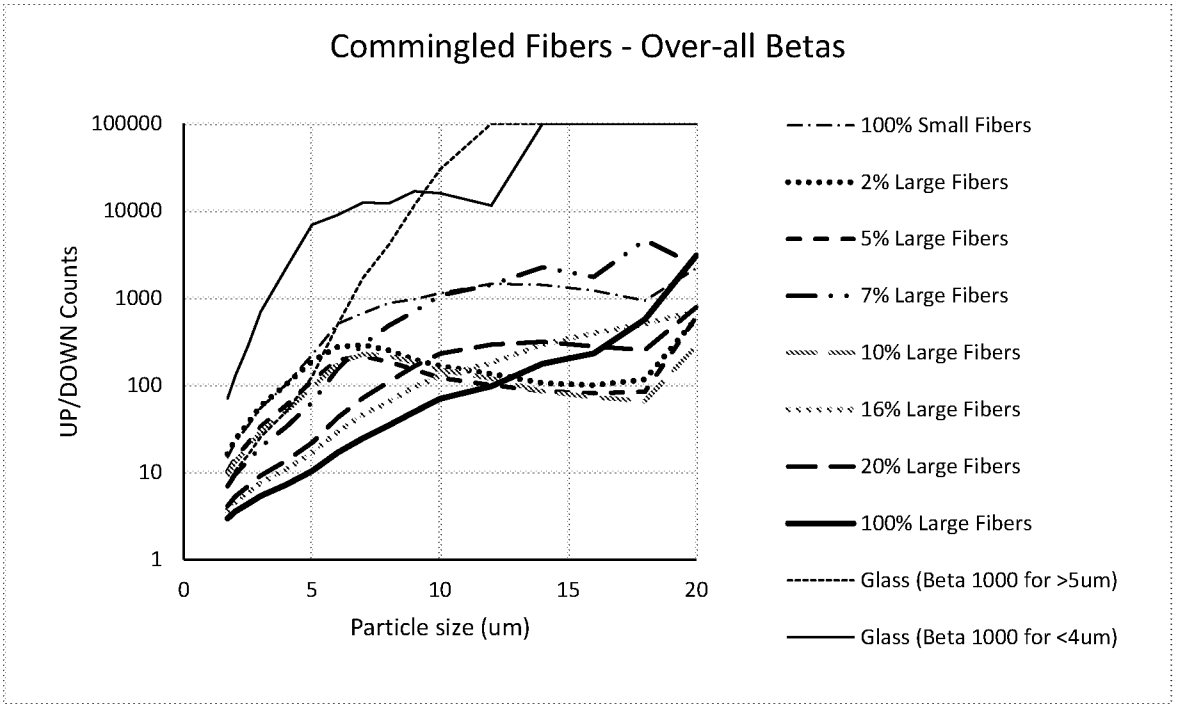

Commingled Fibers - Media dP
Media dP (psi)
Test Time (min)
0
0.5
1
1.5
2
2.5
3
0
2
4
6
8
10
100% Small Fibers
2% Large Fibers
5% Large Fibers
7% Large Fibers
10% Large Fibers
16% Large Fibers
20% Large Fibers
100% Large Fibers
Glass (Beta 1000 for >5um)
Glass (Beta 1000 for <4um)

FIG. 5H


Commingled Fibers - Over-all Betas
UP/DOWN Counts
100000
10000
1000
100
10
1
0
5
10
15
20
Particle size (um)
100% Small Fibers
2% Large Fibers
5% Large Fibers
7% Large Fibers
10% Large Fibers
16% Large Fibers
20% Large Fibers
100% Large Fibers
Glass (Beta 1000 for >5um)
Glass (Beta 1000 for <4um)

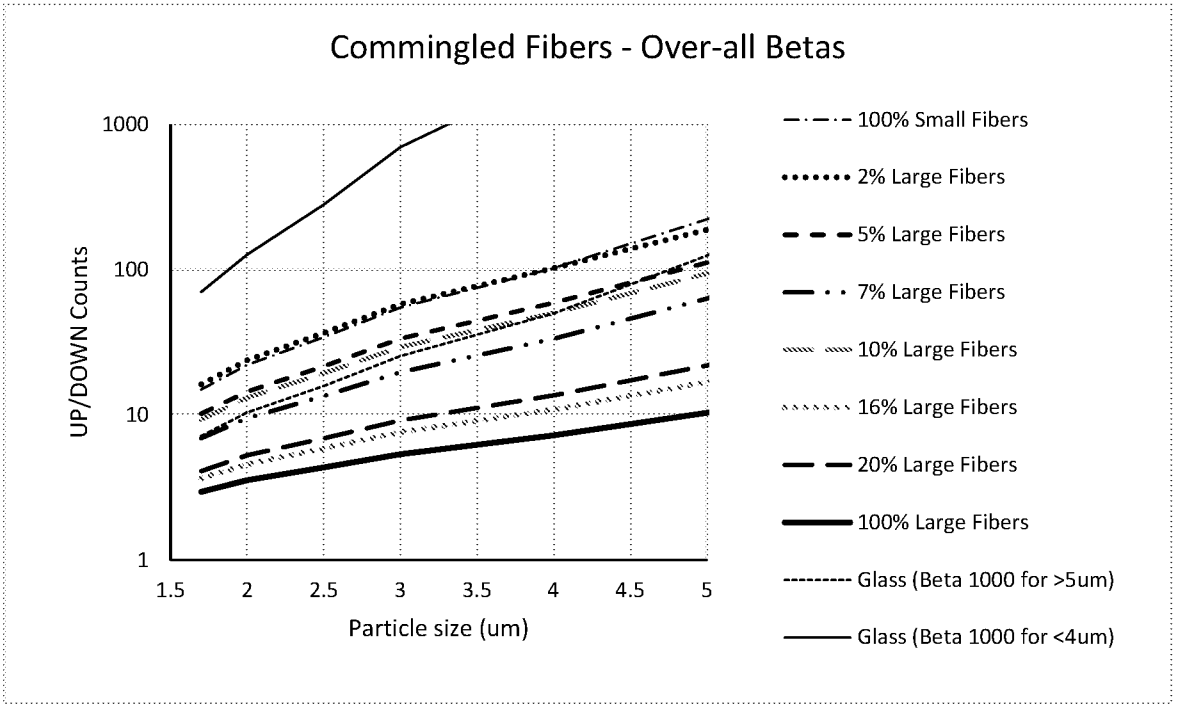
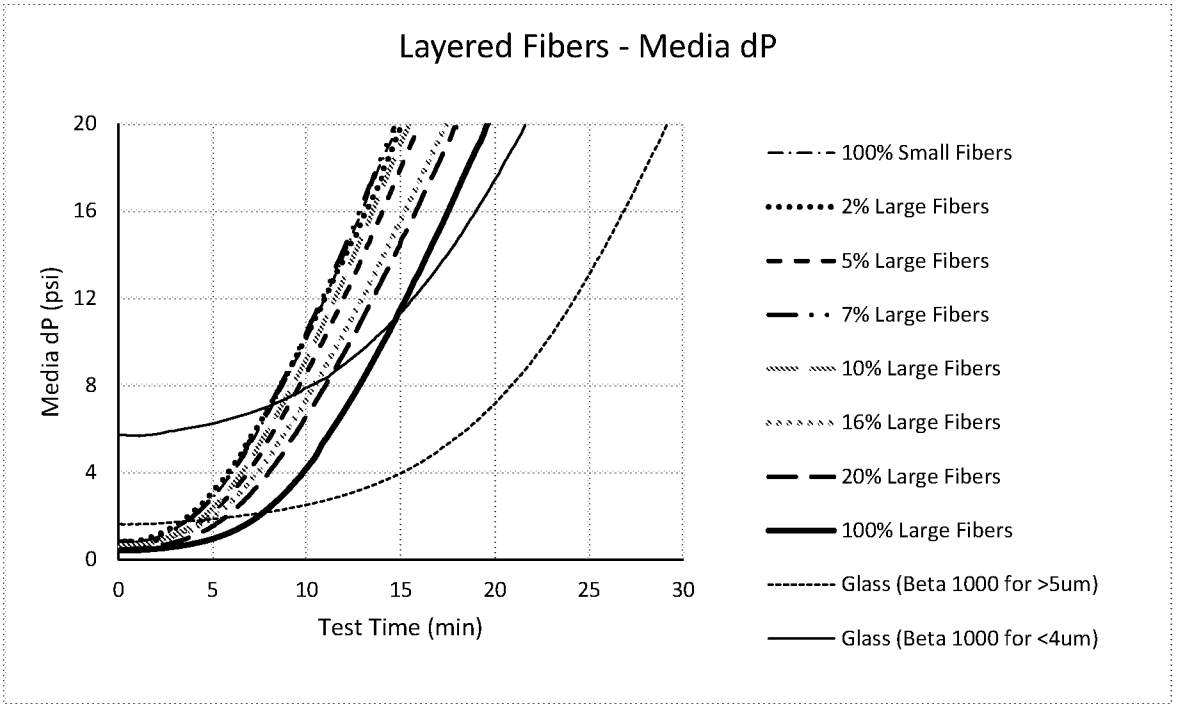

Commingled Fibers - Over-all Betas
UP/DOWN Counts
1000
100
10
1
1.5
2
2.5
3
3.5
4
4.5
5
Particle size (um)
100% Small Fibers
2% Large Fibers
5% Large Fibers
7% Large Fibers
10% Large Fibers
16% Large Fibers
20% Large Fibers
100% Large Fibers
Glass (Beta 1000 for >5um)
Glass (Beta 1000 for <4um)

FIG. 5I


Layered Fibers - Media dP
Media dP (psi)
Test Time (min)
0
4
8
12
16
20
0
5
10
15
20
25
30
100% Small Fibers
2% Large Fibers
5% Large Fibers
7% Large Fibers
10% Large Fibers
16% Large Fibers
20% Large Fibers
100% Large Fibers
Glass (Beta 1000 for >5um)
Glass (Beta 1000 for <4um)

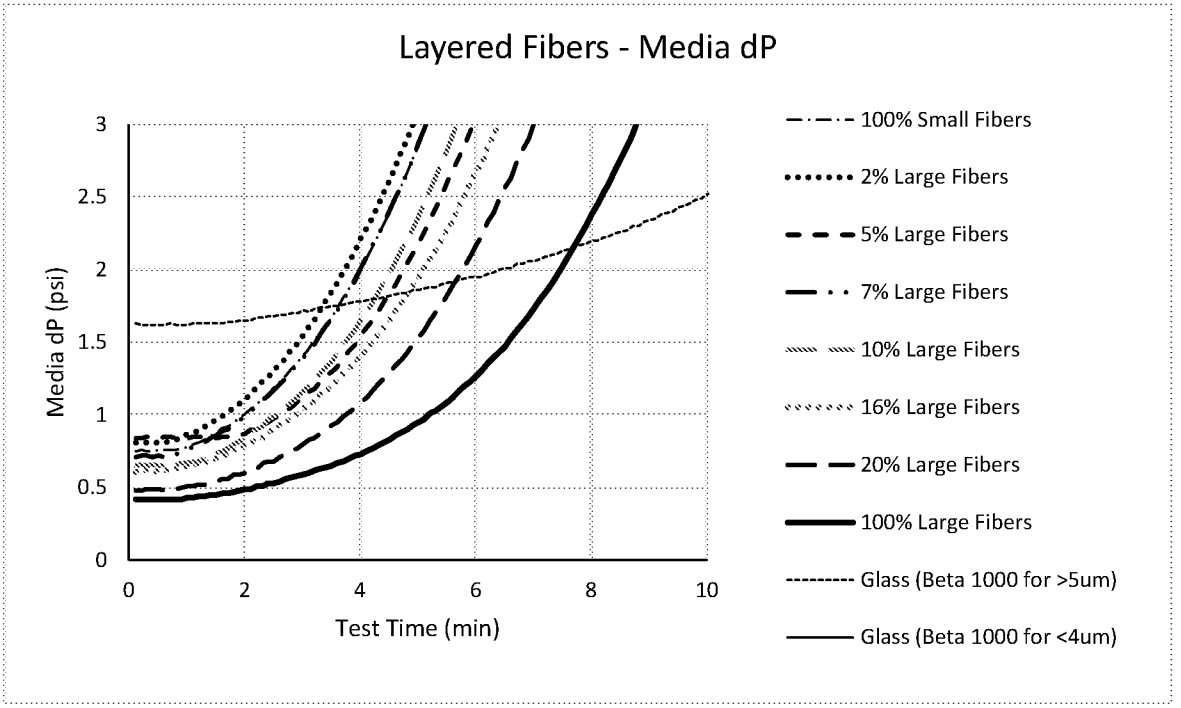
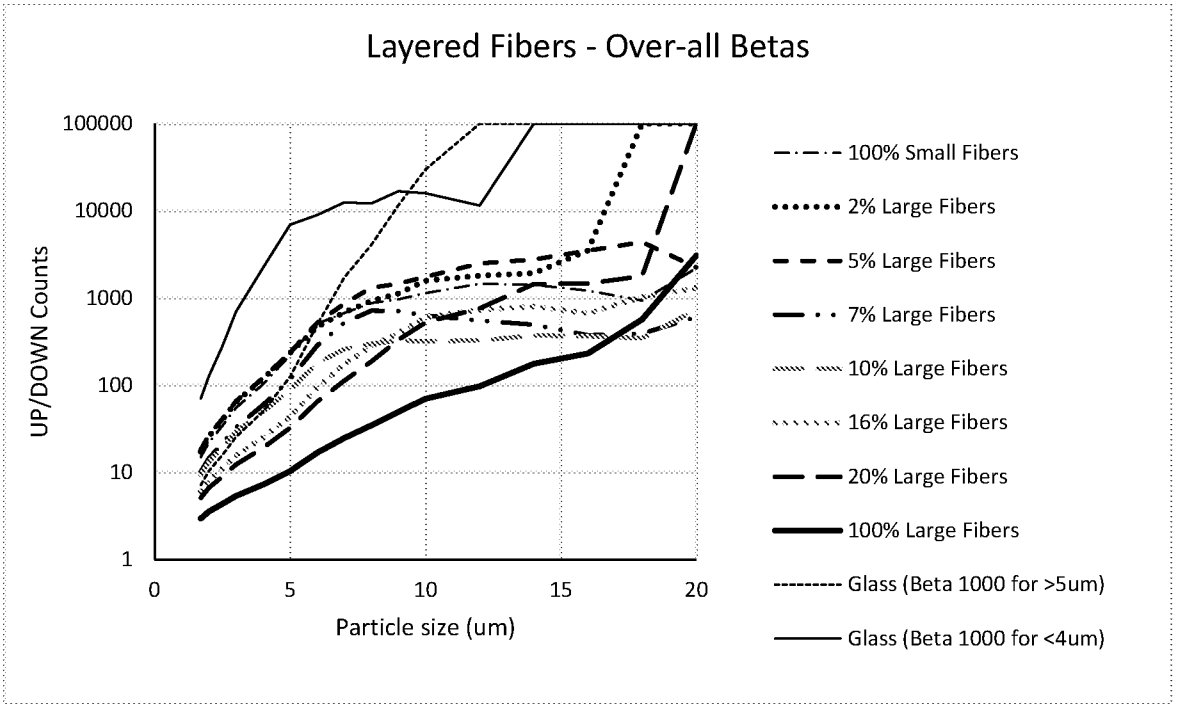

Layered Fibers - Media dP
Media dP (psi)
Test Time (min)
0
0.5
1
1.5
2
2.5
3
0
2
4
6
8
10
100% Small Fibers
2% Large Fibers
5% Large Fibers
7% Large Fibers
10% Large Fibers
16% Large Fibers
20% Large Fibers
100% Large Fibers
Glass (Beta 1000 for >5um)
Glass (Beta 1000 for <4um)

FIG. 5J


Layered Fibers - Over-all Betas
UP/DOWN Counts
100000
10000
1000
100
10
1
0
5
10
15
20
Particle size (um)
100% Small Fibers
2% Large Fibers
5% Large Fibers
7% Large Fibers
10% Large Fibers
16% Large Fibers
20% Large Fibers
100% Large Fibers
Glass (Beta 1000 for >5um)
Glass (Beta 1000 for <4um)

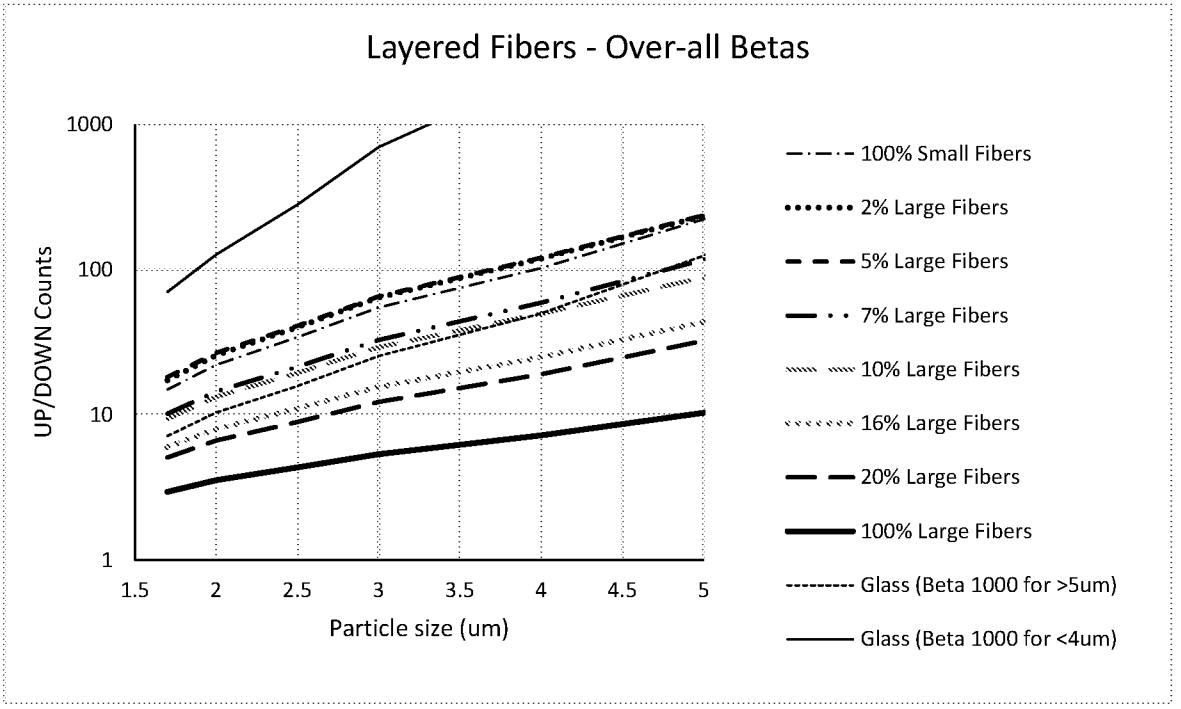

Layered Fibers - Over-all Betas
UP/DOWN Counts
1000
100
10
1
1.5
2
2.5
3
3.5
4
4.5
5
Particle size (um)
100% Small Fibers
2% Large Fibers
5% Large Fibers
7% Large Fibers
10% Large Fibers
16% Large Fibers
20% Large Fibers
100% Large Fibers
Glass (Beta 1000 for >5um)
Glass (Beta 1000 for <4um)

FIG. 5K

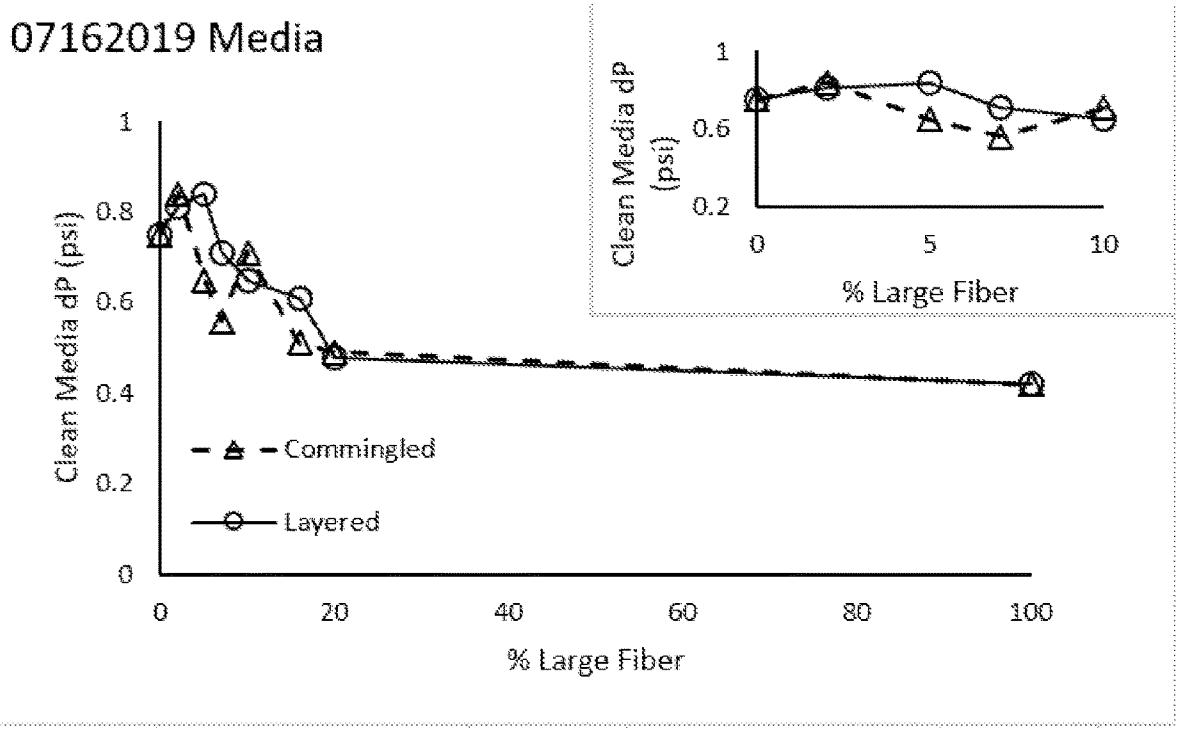

07162019 Media
Clean Media dP (psi)
1
0.8
0.6
0.4
0.2
0
0
20
40
60
80
100
% Large Fiber
Commingled
Layered
Clean Media dP (psi)
1
0.6
0.2
0
5
10
% Large Fiber

FIG. 6A

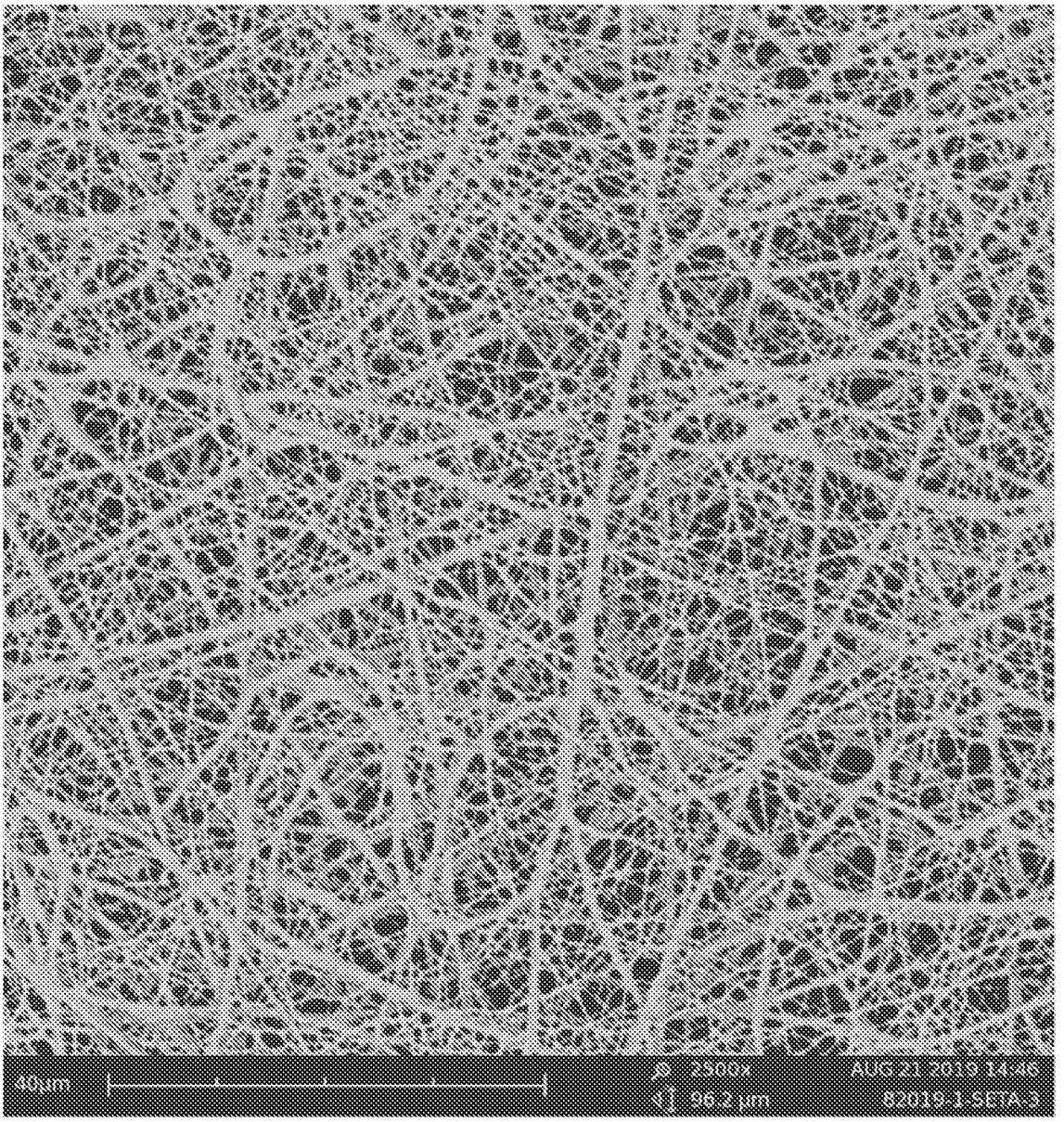


FIG. 6B

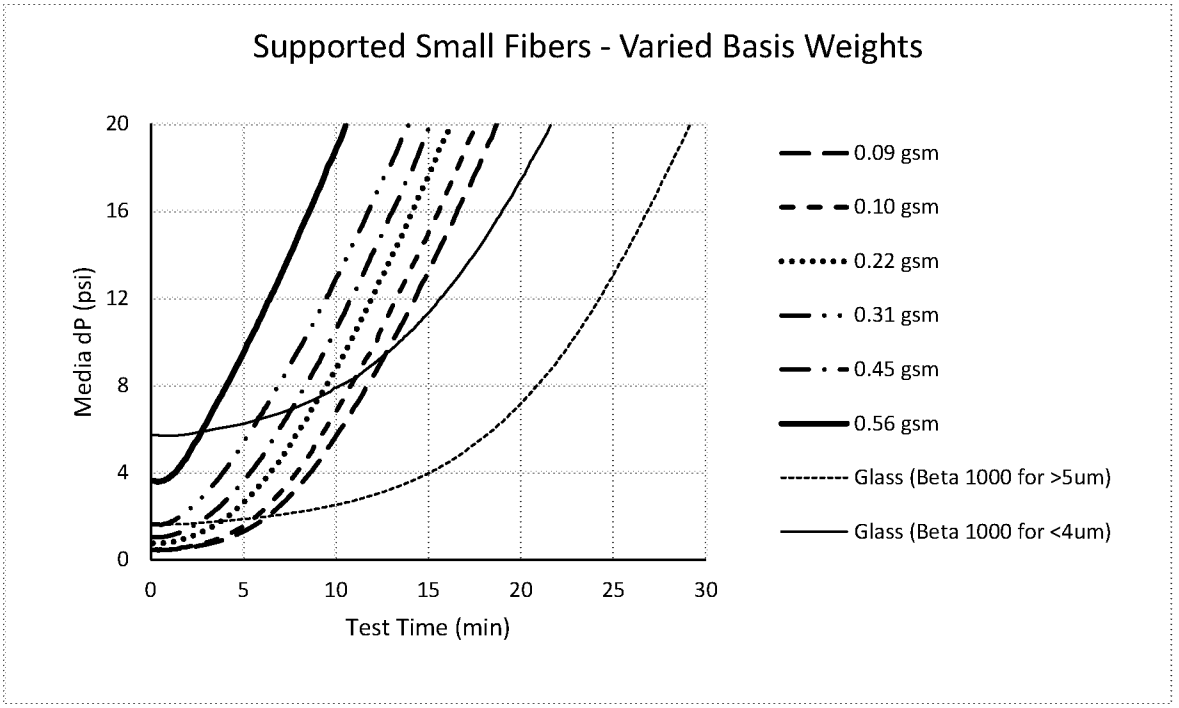

Supported Small Fibers - Varied Basis Weights
Media dP (psi)
0
4
8
12
16
20
0
5
10
15
20
25
30
Test Time (min)
0.09 gsm
0.10 gsm
0.22 gsm
0.31 gsm
0.45 gsm
0.56 gsm
Glass (Beta 1000 for >5um)
Glass (Beta 1000 for <4um)

FIG. 6C

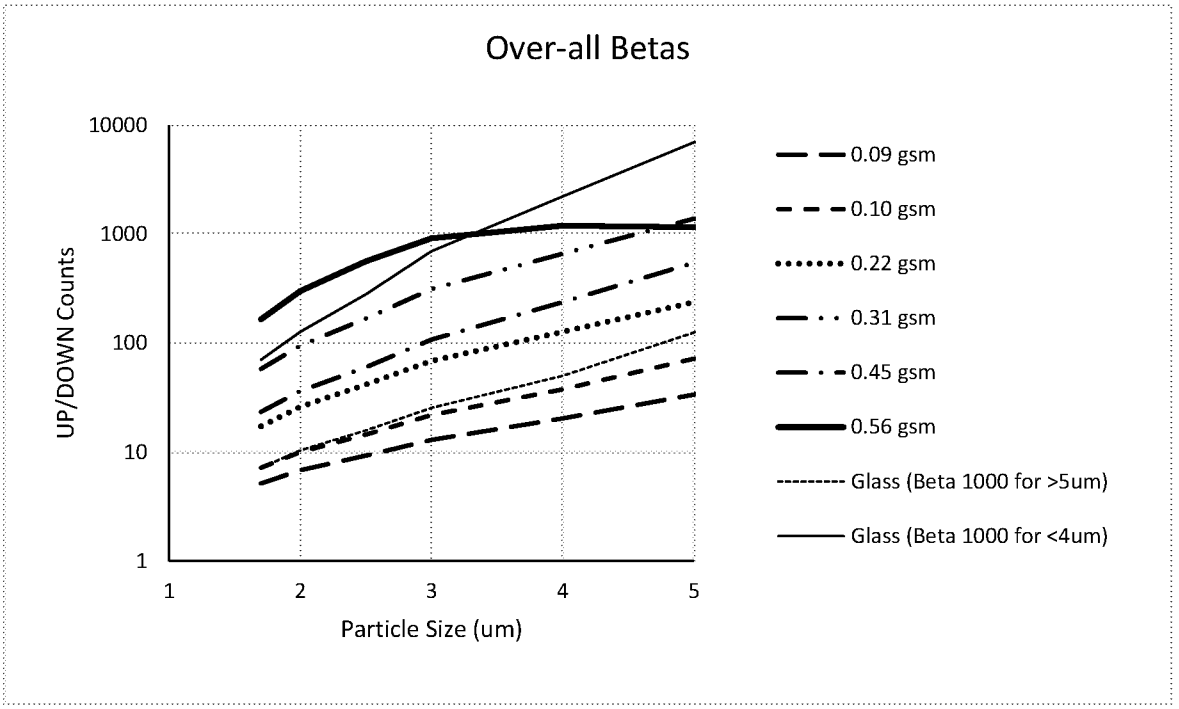

Over-all Betas
UP/DOWN Counts
1
10
100
1000
10000
1
2
3
4
5
Particle Size (um)
0.09 gsm
0.10 gsm
0.22 gsm
0.31 gsm
0.45 gsm
0.56 gsm
Glass (Beta 1000 for >5um)
Glass (Beta 1000 for <4um)

FIG. 7A

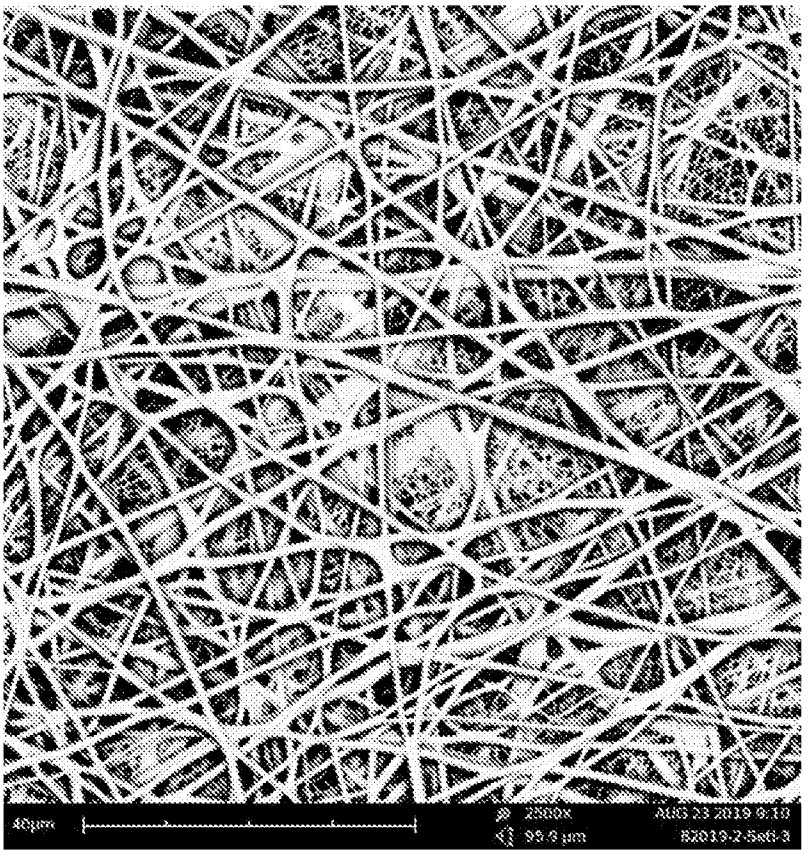

40μm
2500x
95.9 μm
AUG 23 2019 9:10
82019-2-Set1-3

FIG. 7B

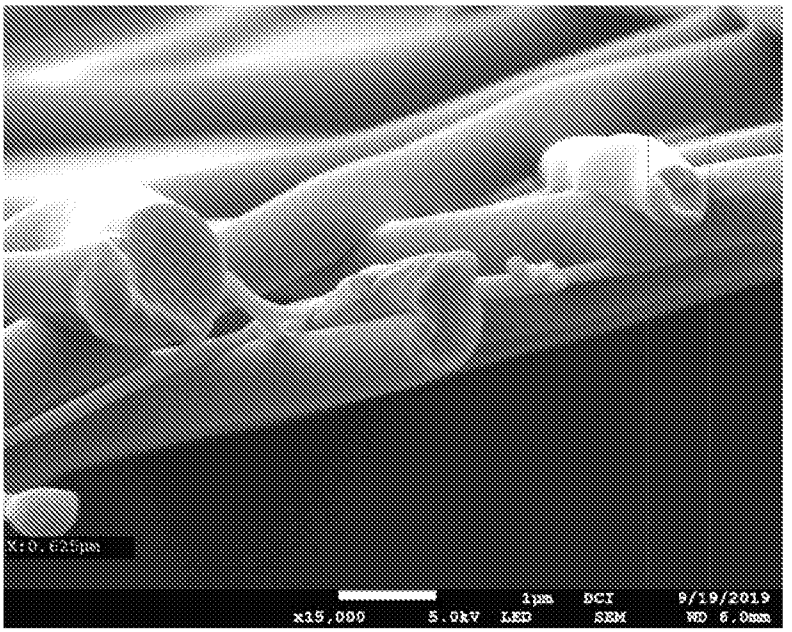

X:0.625μm
1μm
DCI
9/19/2019
x15,000
5.0kV
LED
SEM
WD 6.0mm

FIG. 7C

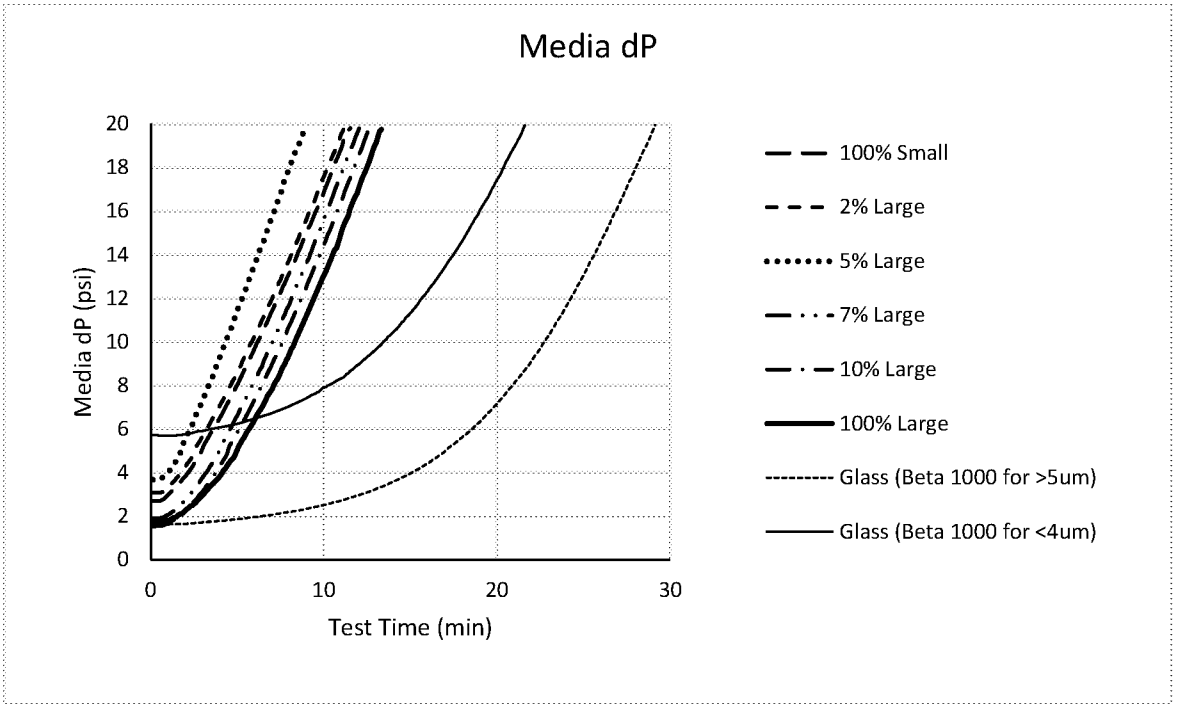

Media dP
Media dP (psi)
0
2
4
6
8
10
12
14
16
18
20
0
10
20
30
Test Time (min)
100% Small
2% Large
5% Large
7% Large
10% Large
100% Large
Glass (Beta 1000 for >5um)
Glass (Beta 1000 for <4um)

FIG. 7D

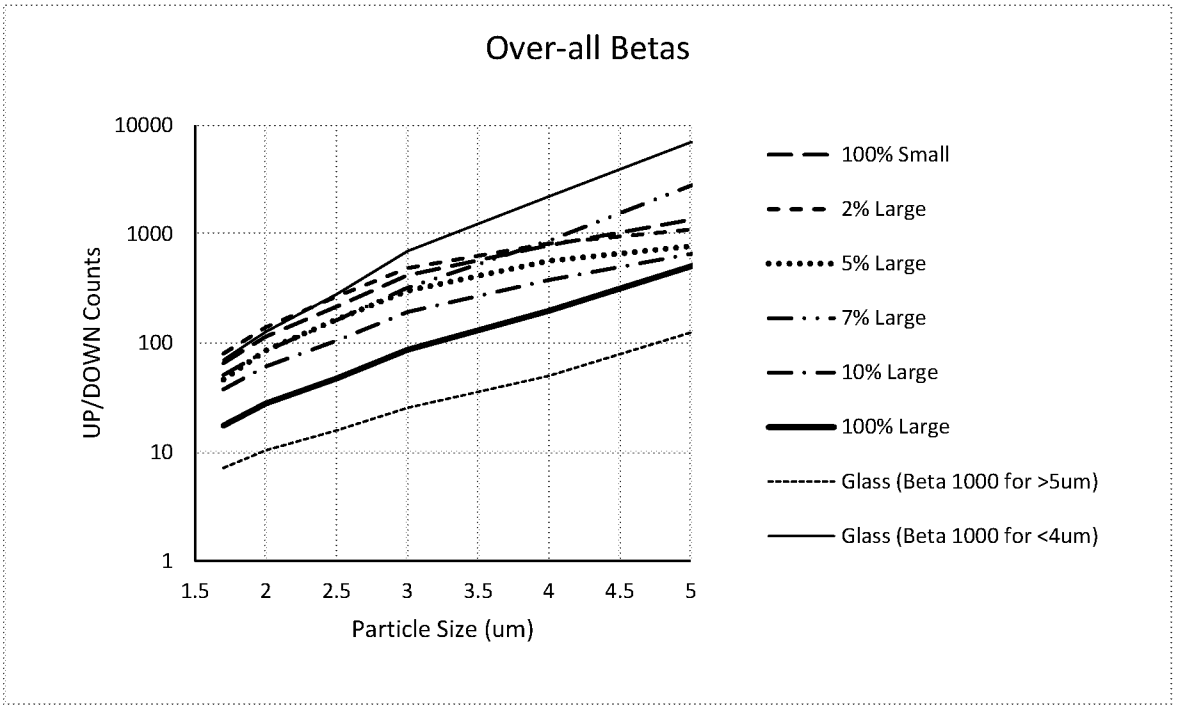

Over-all Betas
UP/DOWN Counts
1
10
100
1000
10000
1.5
2
2.5
3
3.5
4
4.5
5
Particle Size (um)
100% Small
2% Large
5% Large
7% Large
10% Large
100% Large
Glass (Beta 1000 for >5um)
Glass (Beta 1000 for <4um)

FIG. 8A

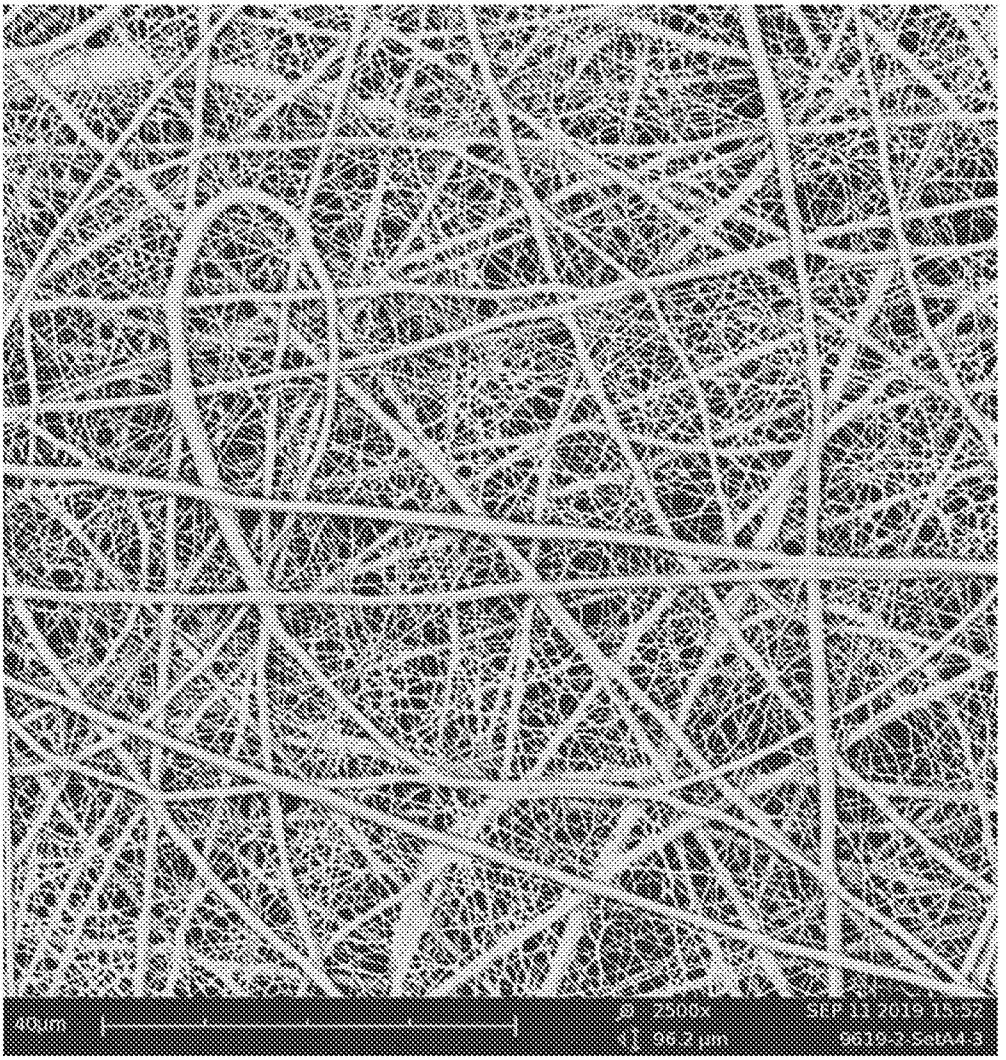


FIG. 8B

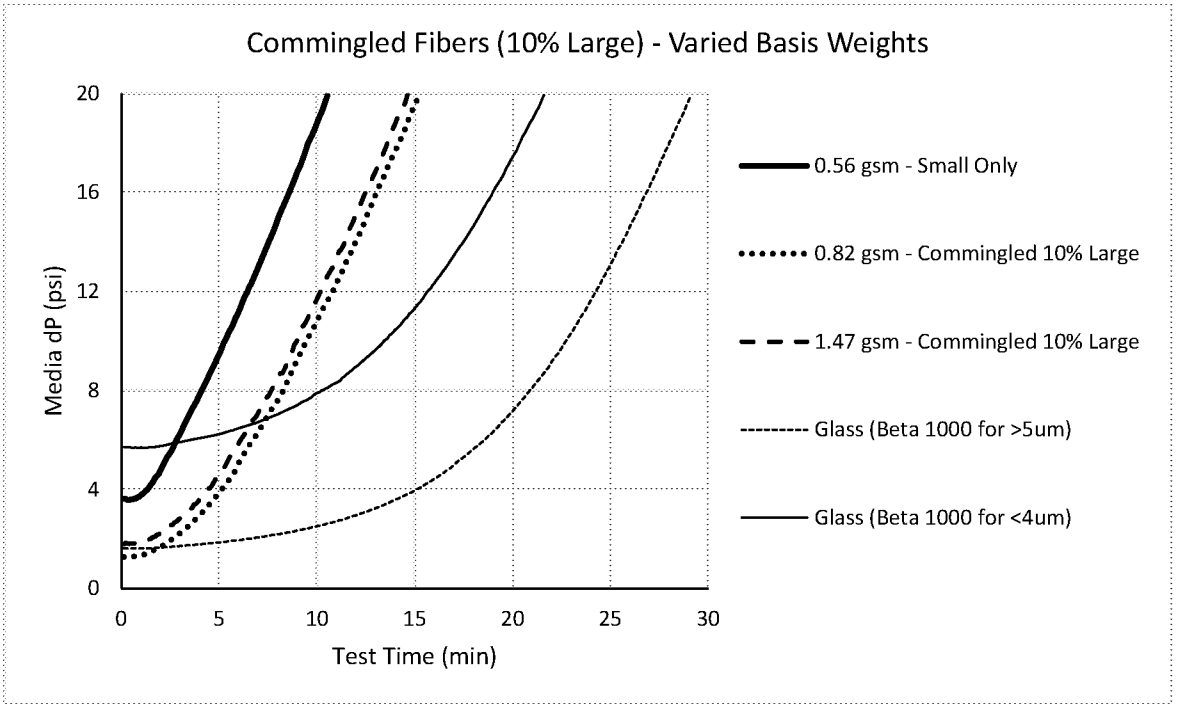

Commingled Fibers (10% Large) - Varied Basis Weights
Media dP (psi)
20
16
12
8
4
0
0
5
10
15
20
25
30
Test Time (min)
0.56 gsm - Small Only
0.82 gsm - Commingled 10% Large
1.47 gsm - Commingled 10% Large
Glass (Beta 1000 for >5um)
Glass (Beta 1000 for <4um)

FIG. 8C

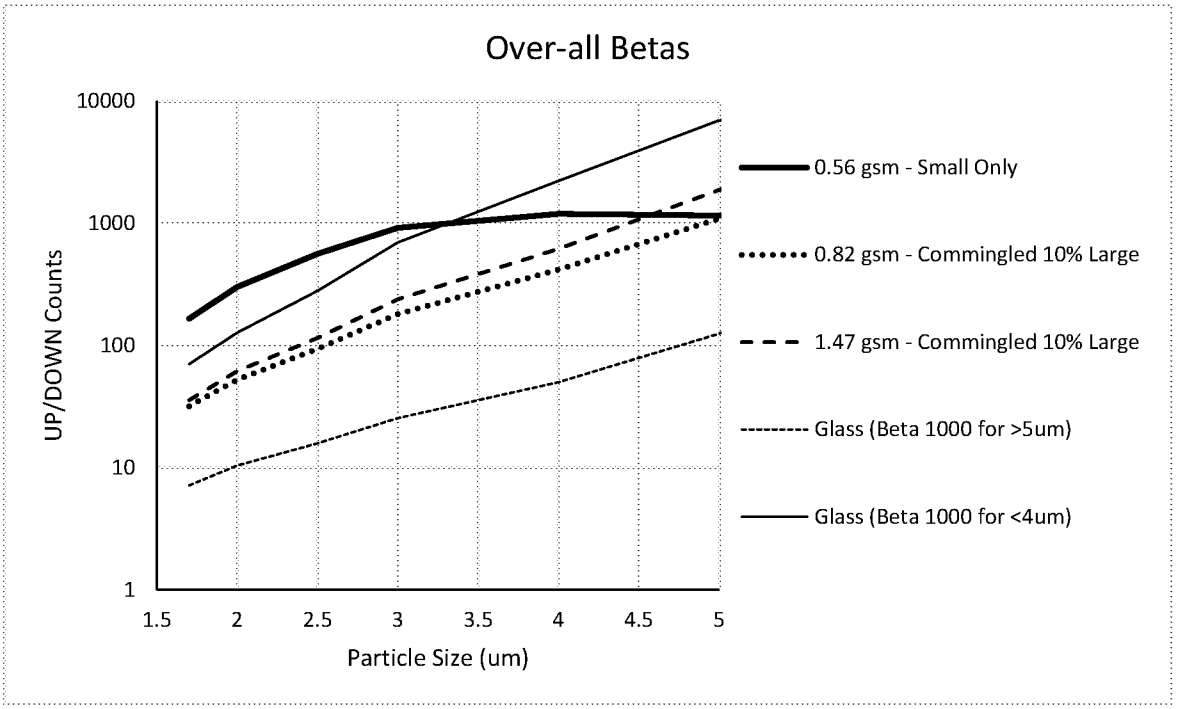

Over-all Betas
UP/DOWN Counts
10000
1000
100
10
1
1.5
2
2.5
3
3.5
4
4.5
5
Particle Size (um)
0.56 gsm - Small Only
0.82 gsm - Commingled 10% Large
1.47 gsm - Commingled 10% Large
Glass (Beta 1000 for >5um)
Glass (Beta 1000 for <4um)

FIG. 9A

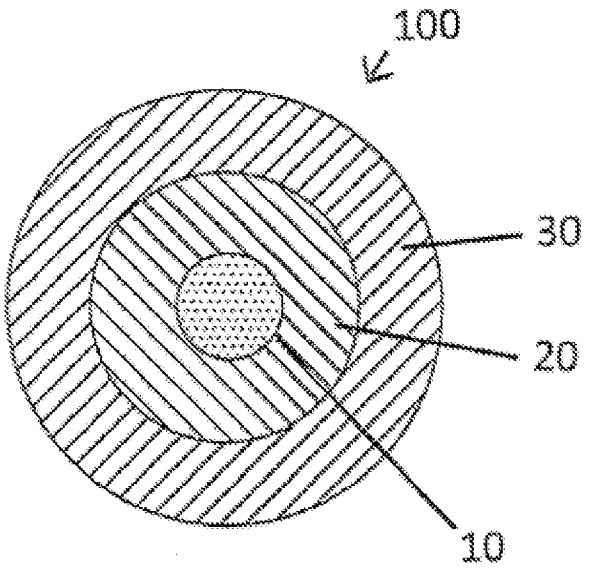



FIG. 9B

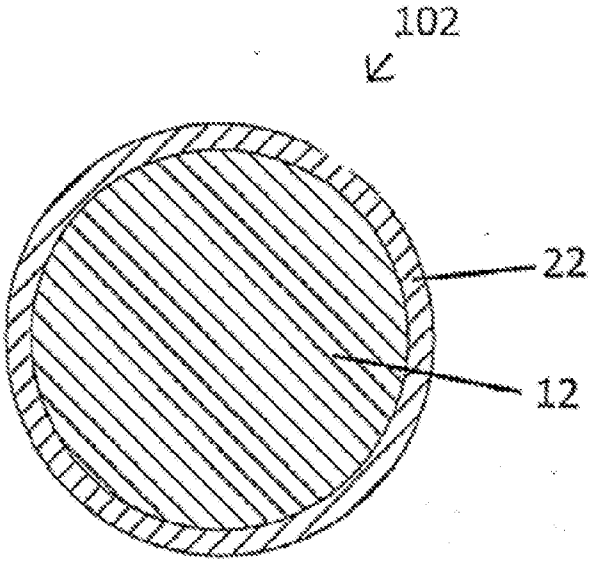


FIG. 10A

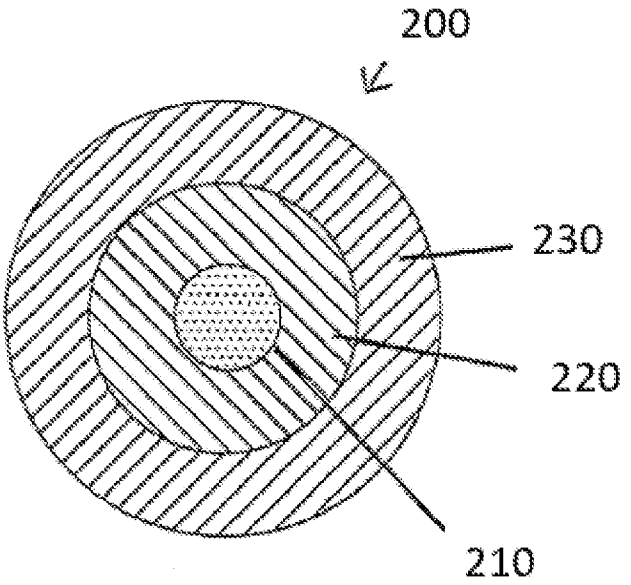



FIG. 10B

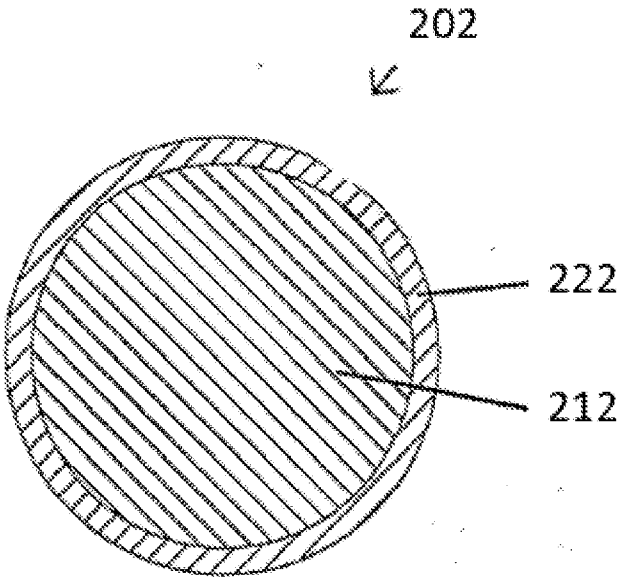


FIG. 11A

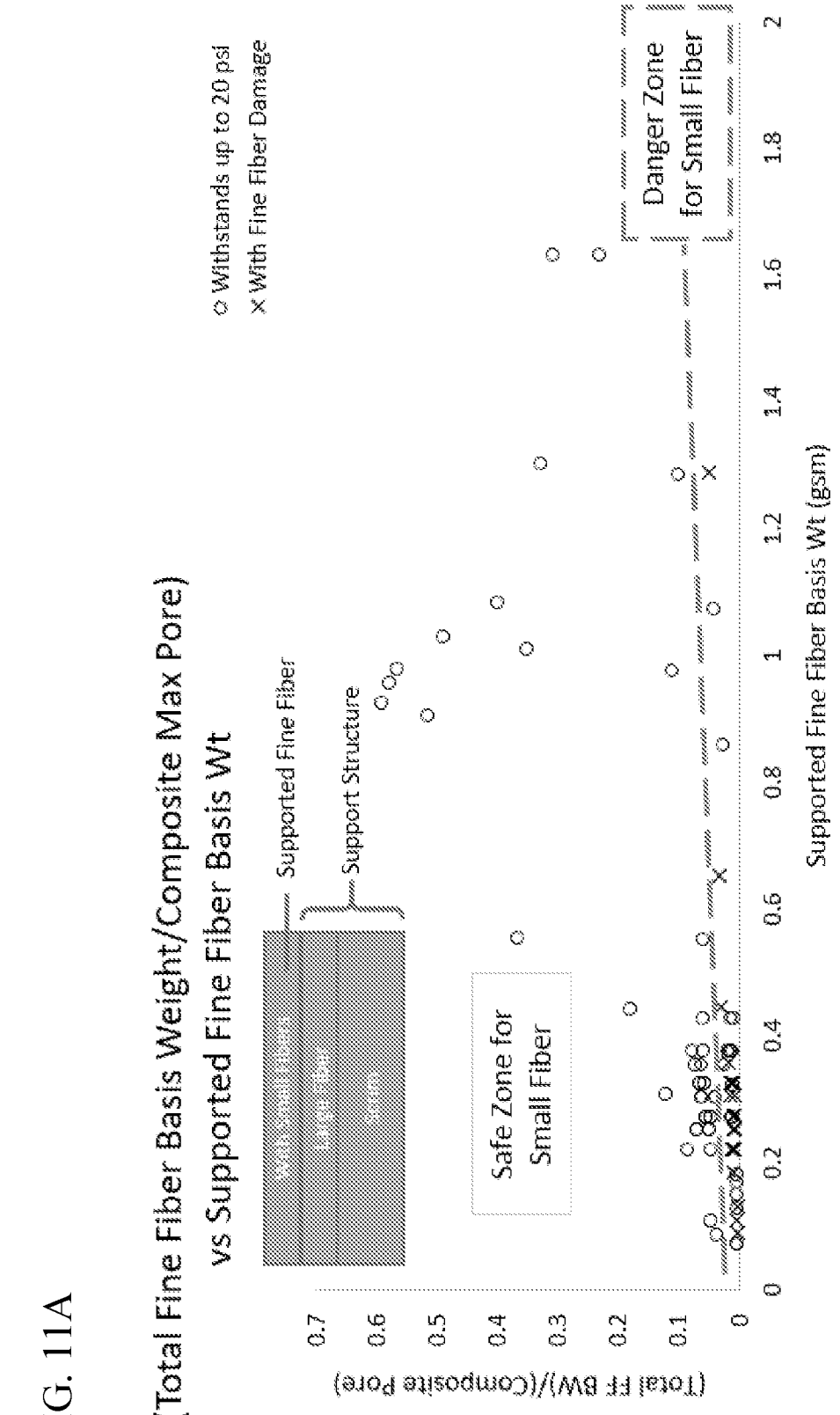

(Total Fine Fiber Basis Weight/Composite Max Pore)
vs Supported Fine Fiber Basis Wt
◇ Withstands up to 20 psi
× With Fine Fiber Damage
Supported Fine Fiber
Support Structure
Safe Zone for Small Fiber
Danger Zone for Small Fiber
(Total FF BW)/(Composite Pore)
Supported Fine Fiber Basis Wt (gsm)
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.2
0.4
0.6
0.8
1
1.2
1.4
1.6
1.8
2

FIG. 11B

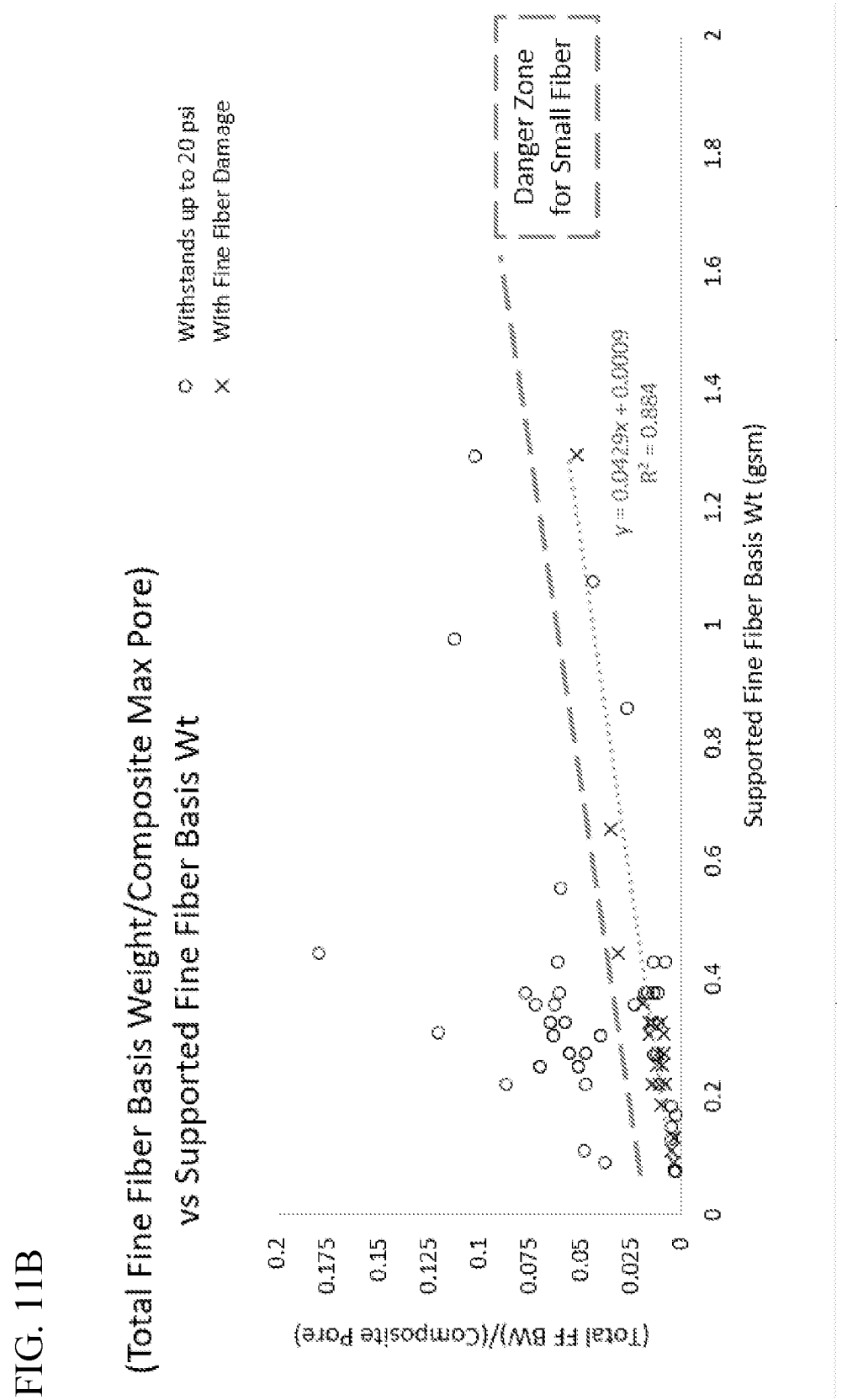

(Total Fine Fiber Basis Weight/Composite Max Pore)
vs Supported Fine Fiber Basis Wt
Withstands up to 20 psi
With Fine Fiber Damage
Danger Zone
for Small Fiber
y = 0.0429x + 0.0009
R² = 0.884
(Total FF BW)/(Composite Pore)
Supported Fine Fiber Basis Wt (gsm)
0
0.025
0.05
0.075
0.1
0.125
0.15
0.175
0.2
0
0.2
0.4
0.6
0.8
1
1.2
1.4
1.6
1.8
2

FIG. 12A

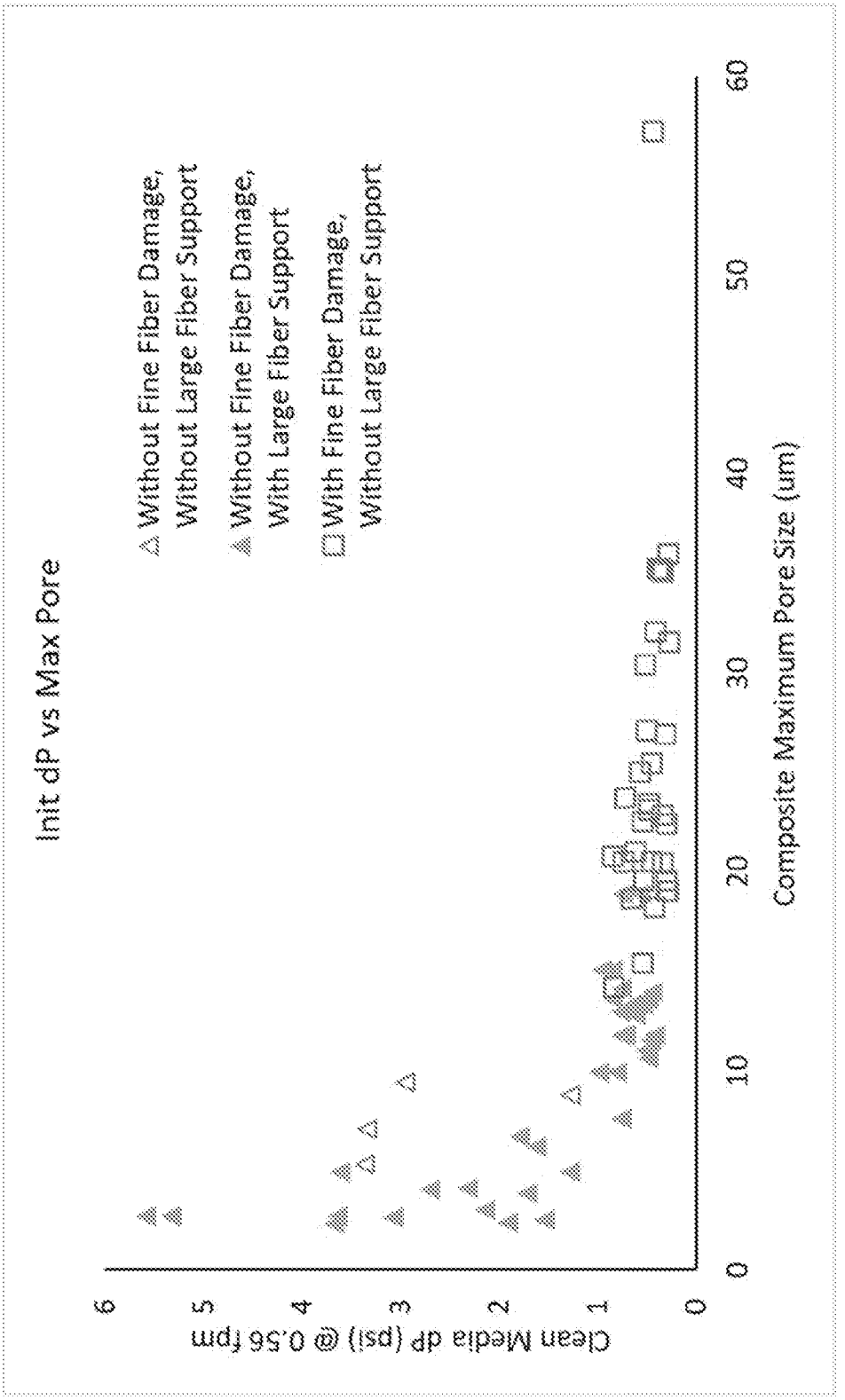
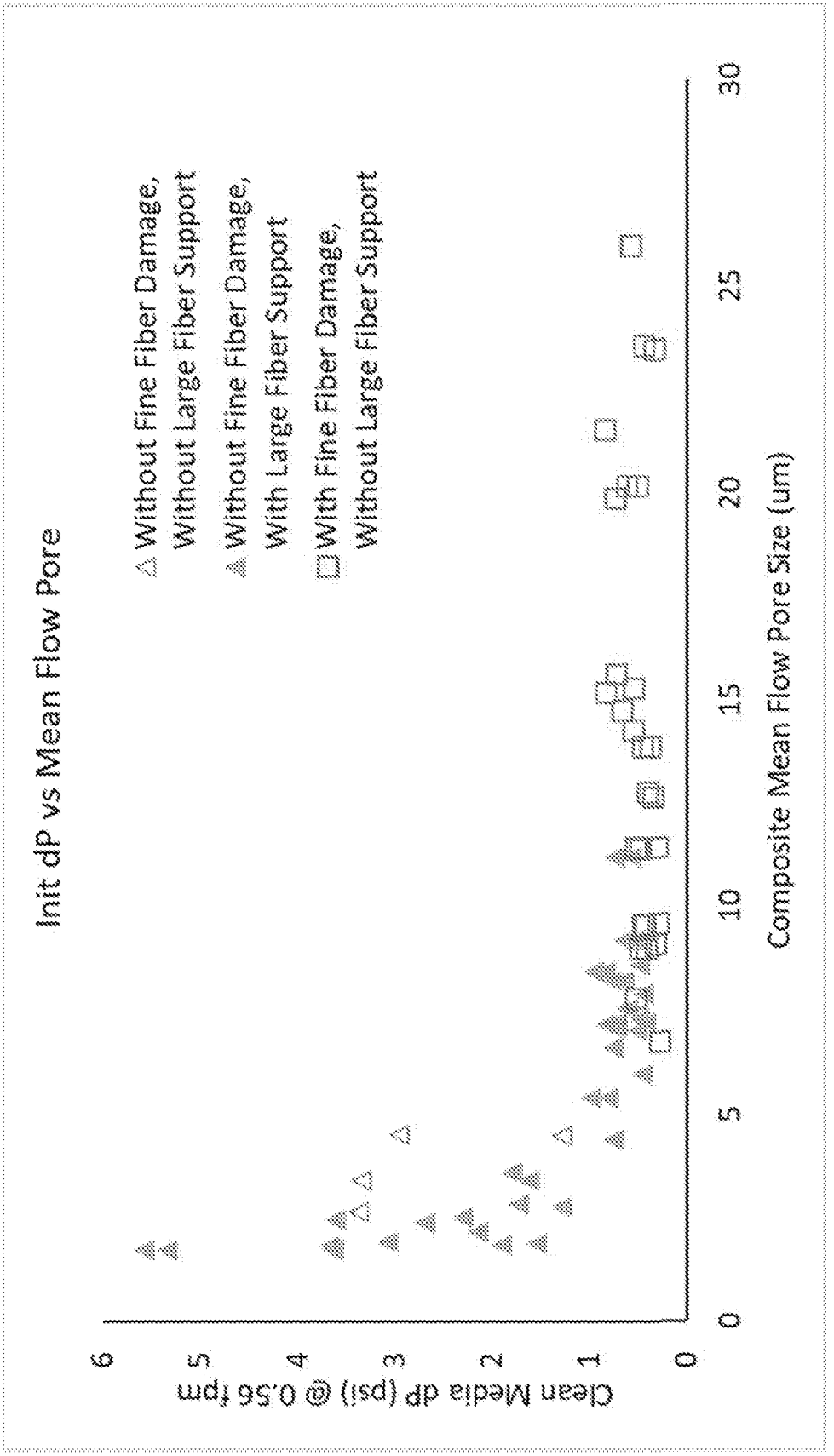

Init dP vs Max Pore
△ Without Fine Fiber Damage, Without Large Fiber Support
▲ Without Fine Fiber Damage, With Large Fiber Support
□ With Fine Fiber Damage, Without Large Fiber Support
Clean Media dP (psi) @ 0.56 fpm
Composite Maximum Pore Size (um)
0
1
2
3
4
5
6
0
10
20
30
40
50
60

FIG. 12B


Init dP vs Mean Flow Pore
Without Fine Fiber Damage, Without Large Fiber Support
Without Fine Fiber Damage, With Large Fiber Support
With Fine Fiber Damage, Without Large Fiber Support
Clean Media dP (psi) @ 0.56 fpm
Composite Mean Flow Pore Size (um)
0
1
2
3
4
5
6
0
5
10
15
20
25
30

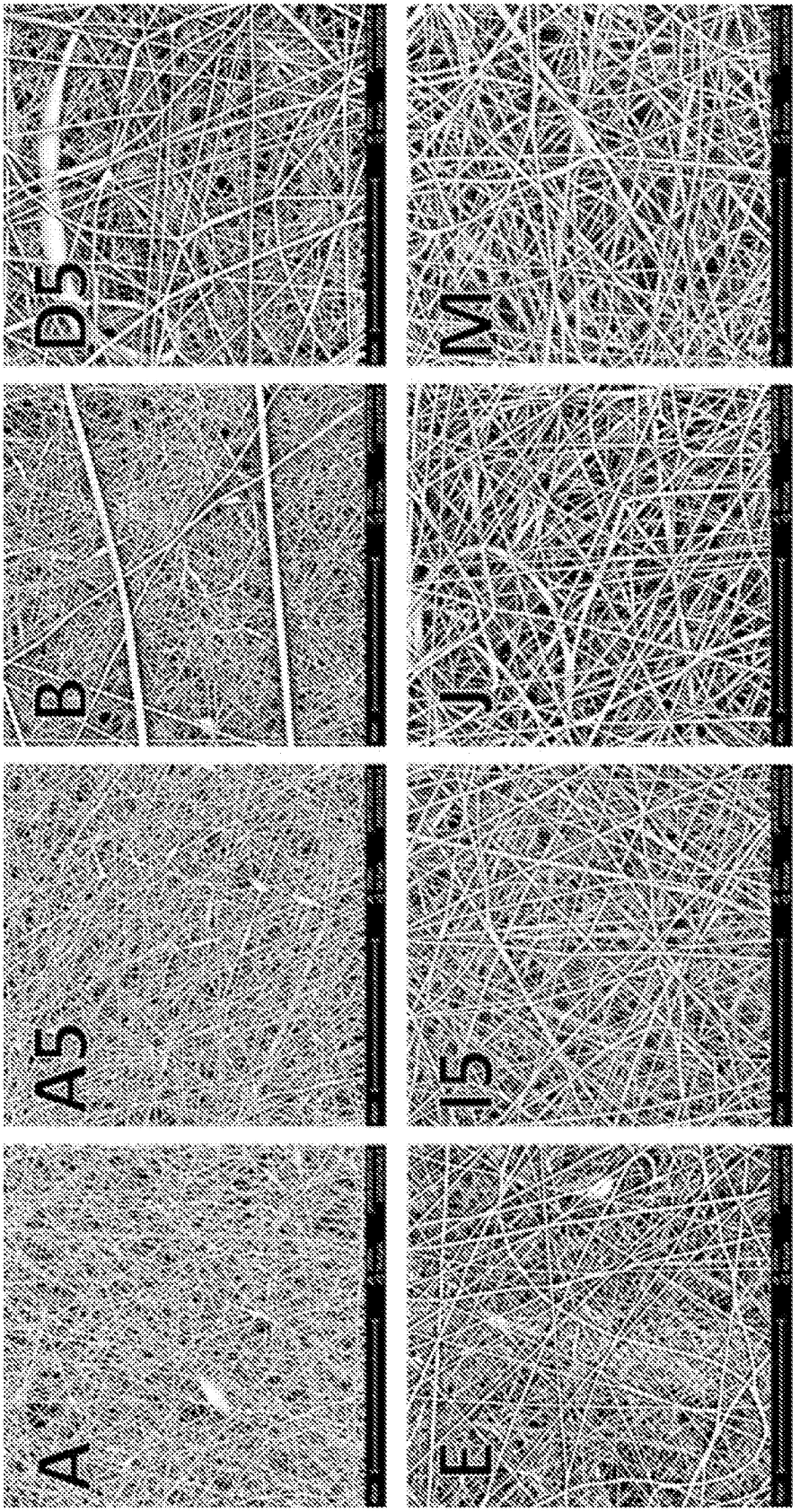



FIG. 13A

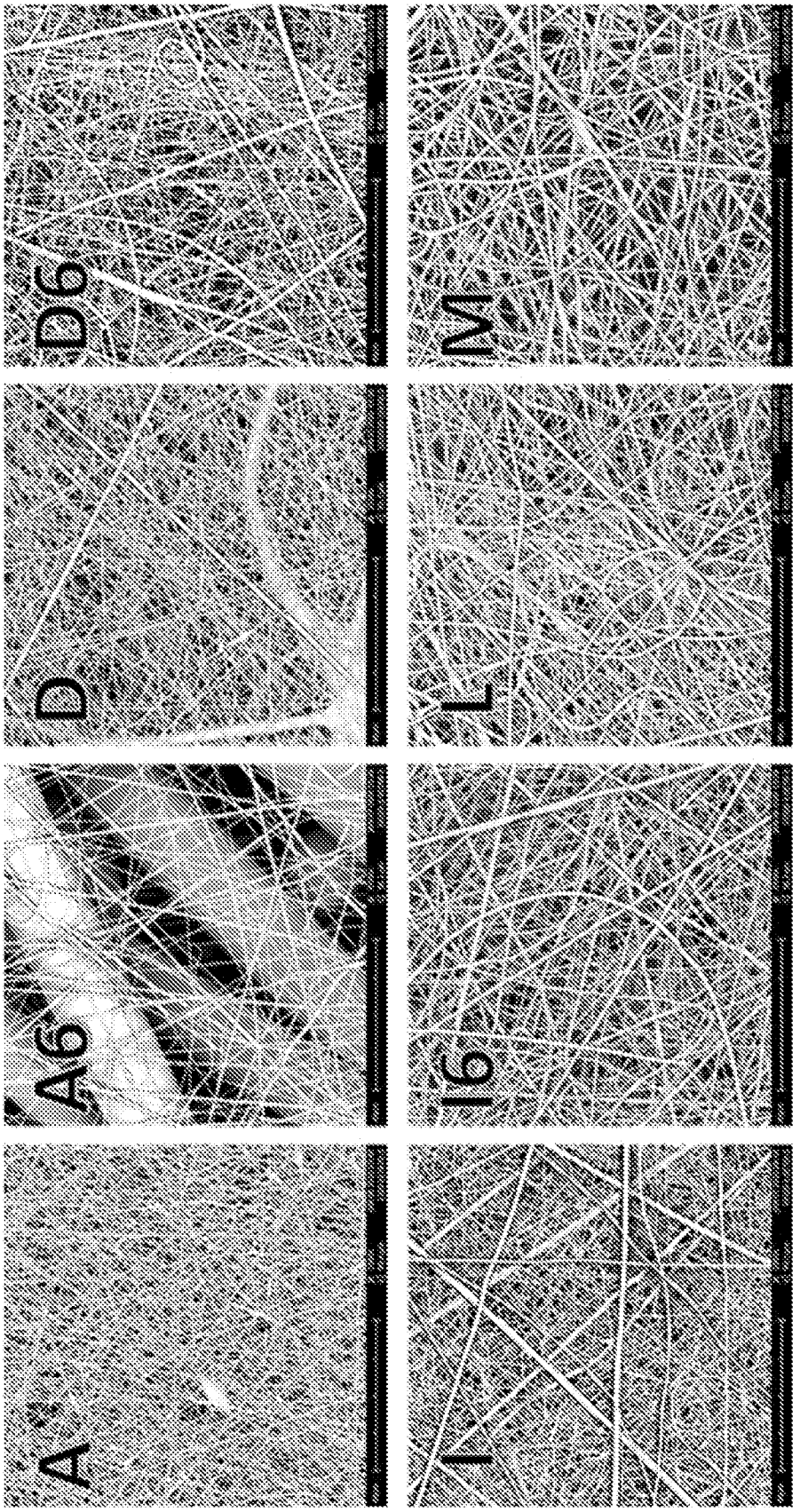



FIG. 13B

FIG. 13C

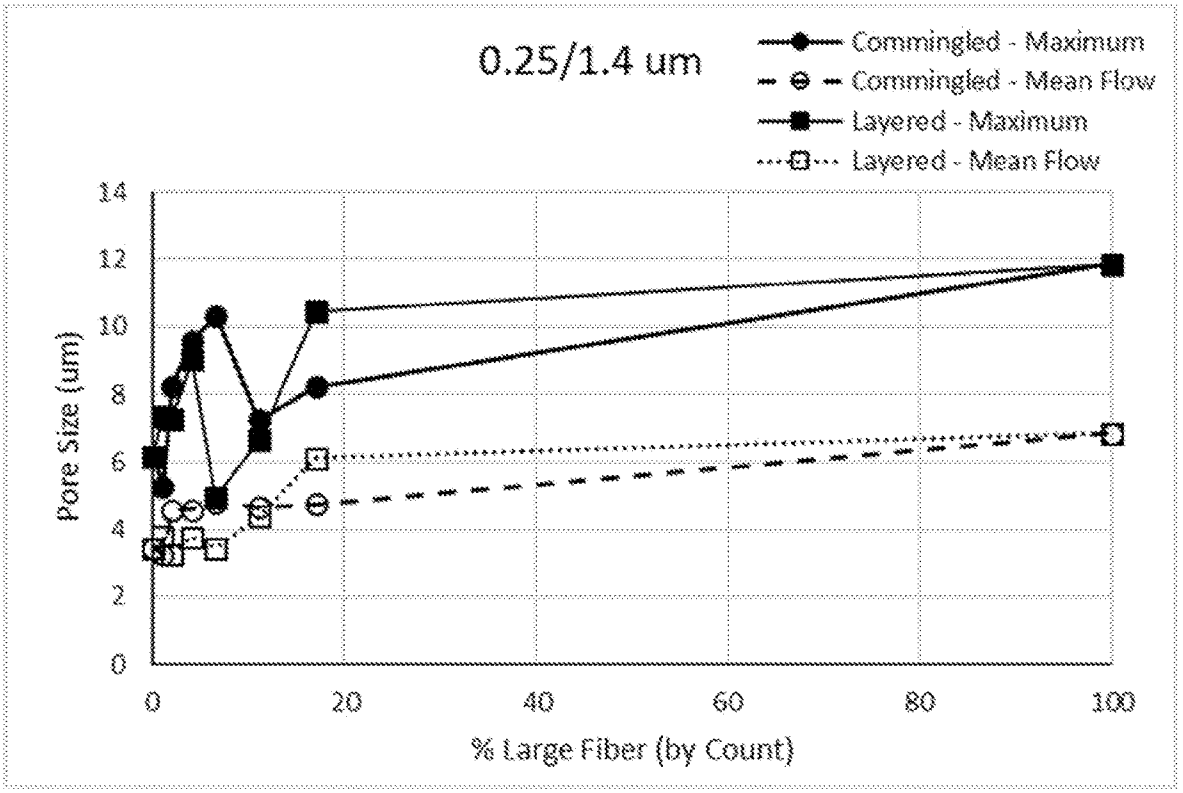
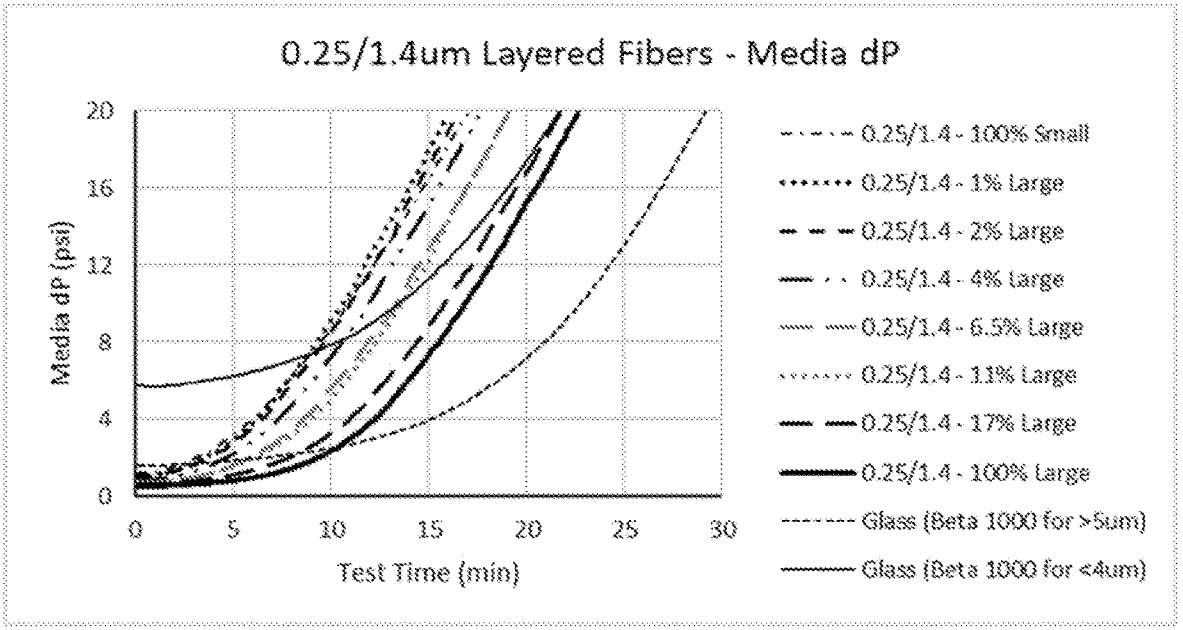

0.25/1.4 um
Commingled - Maximum
Commingled - Mean Flow
Layered - Maximum
Layered - Mean Flow
Pore Size (um)
0
2
4
6
8
10
12
14
0
20
40
60
80
100
% Large Fiber (by Count)

FIG. 13D


0.25/1.4um Layered Fibers - Media dP
Media dP (psi)
Test Time (min)
0.25/1.4 - 100% Small
0.25/1.4 - 1% Large
0.25/1.4 - 2% Large
0.25/1.4 - 4% Large
0.25/1.4 - 6.5% Large
0.25/1.4 - 11% Large
0.25/1.4 - 17% Large
0.25/1.4 - 100% Large
Glass (Beta 1000 for >5um)
Glass (Beta 1000 for <4um)

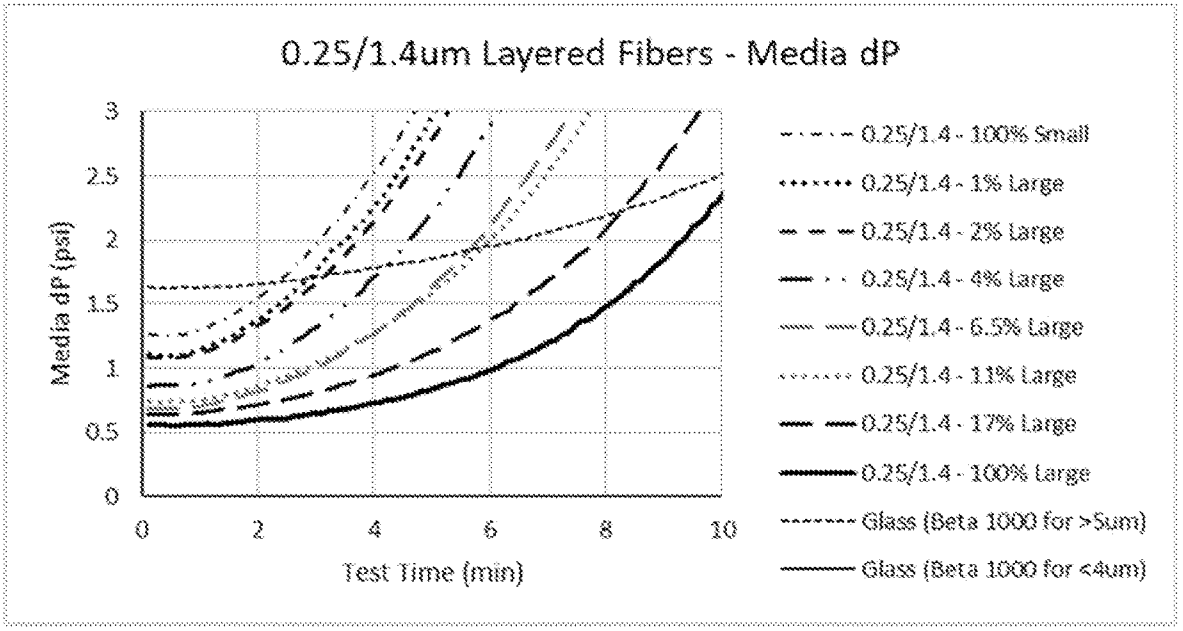
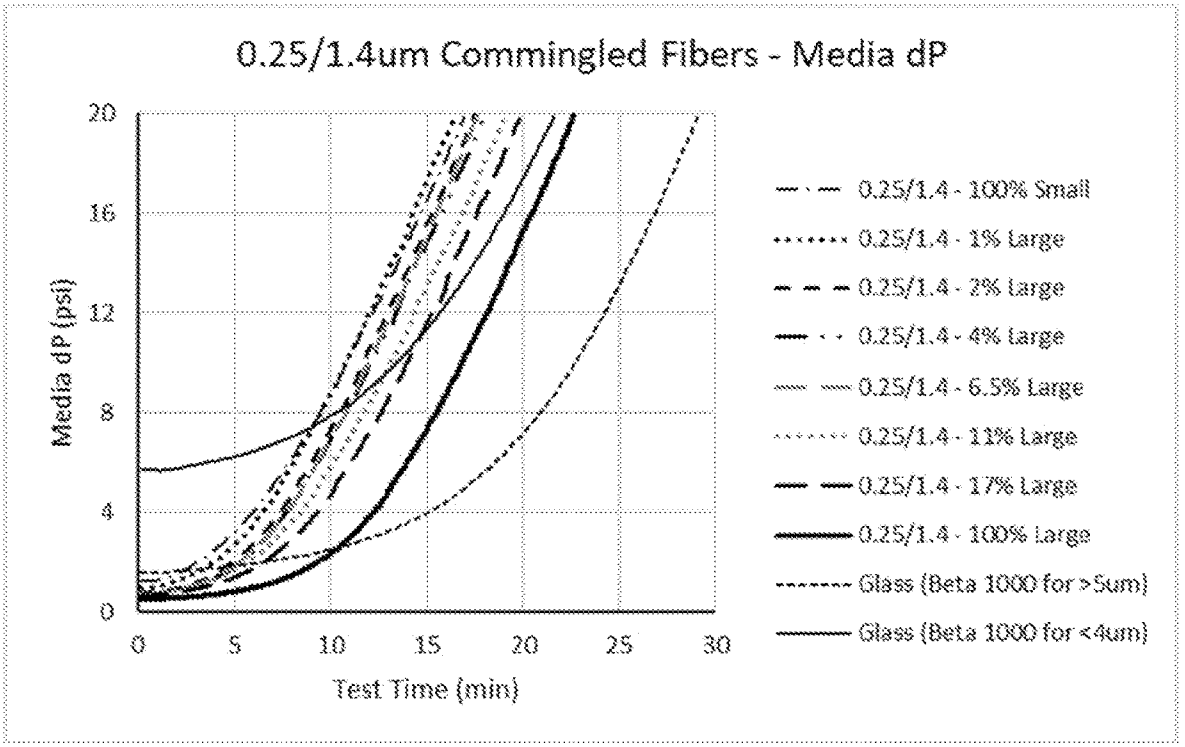

0.25/1.4um Layered Fibers - Media dP
Media dP (psi)
Test Time (min)
0.25/1.4 - 100% Small
0.25/1.4 - 1% Large
0.25/1.4 - 2% Large
0.25/1.4 - 4% Large
0.25/1.4 - 6.5% Large
0.25/1.4 - 11% Large
0.25/1.4 - 17% Large
0.25/1.4 - 100% Large
Glass (Beta 1000 for >5um)
Glass (Beta 1000 for <4um)

FIG. 13E


0.25/1.4um Commingled Fibers - Media dP
Media dP (psi)
Test Time (min)
0.25/1.4 - 100% Small
0.25/1.4 - 1% Large
0.25/1.4 - 2% Large
0.25/1.4 - 4% Large
0.25/1.4 - 6.5% Large
0.25/1.4 - 11% Large
0.25/1.4 - 17% Large
0.25/1.4 - 100% Large
Glass (Beta 1000 for >5um)
Glass (Beta 1000 for <4um)

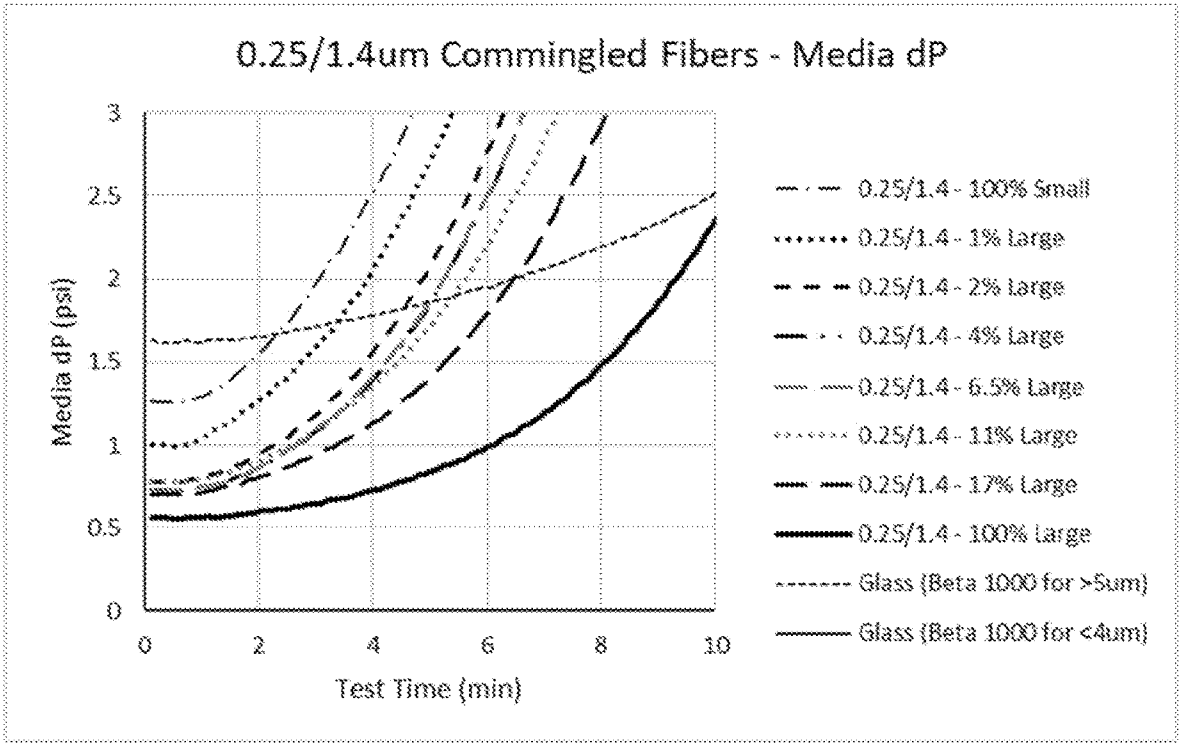
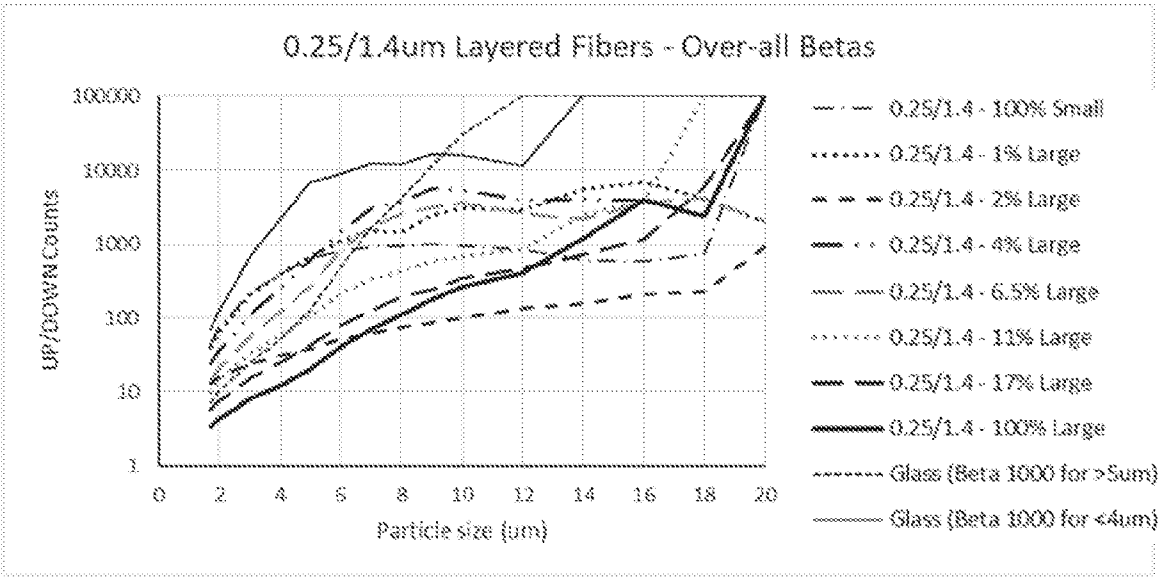

0.25/1.4um Commingled Fibers - Media dP
Media dP (psi)
Test Time (min)
0.25/1.4 - 100% Small
0.25/1.4 - 1% Large
0.25/1.4 - 2% Large
0.25/1.4 - 4% Large
0.25/1.4 - 6.5% Large
0.25/1.4 - 11% Large
0.25/1.4 - 17% Large
0.25/1.4 - 100% Large
Glass (Beta 1000 for >5um)
Glass (Beta 1000 for <4um)

FIG. 13F


0.25/1.4um Layered Fibers - Over-all Betas
UP/DOWN Counts
100000
10000
1000
100
10
1
0
2
4
6
8
10
12
14
16
18
20
Particle size (um)
0.25/1.4 - 100% Small
0.25/1.4 - 1% Large
0.25/1.4 - 2% Large
0.25/1.4 - 4% Large
0.25/1.4 - 6.5% Large
0.25/1.4 - 11% Large
0.25/1.4 - 17% Large
0.25/1.4 - 100% Large
Glass (Beta 1000 for >Sum)
Glass (Beta 1000 for <4um)

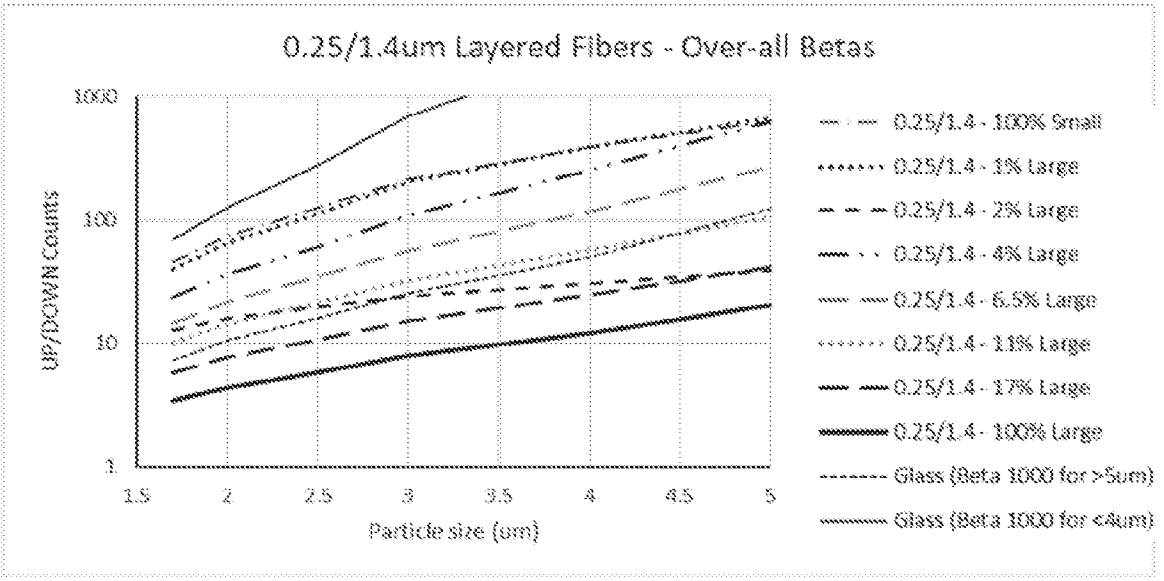
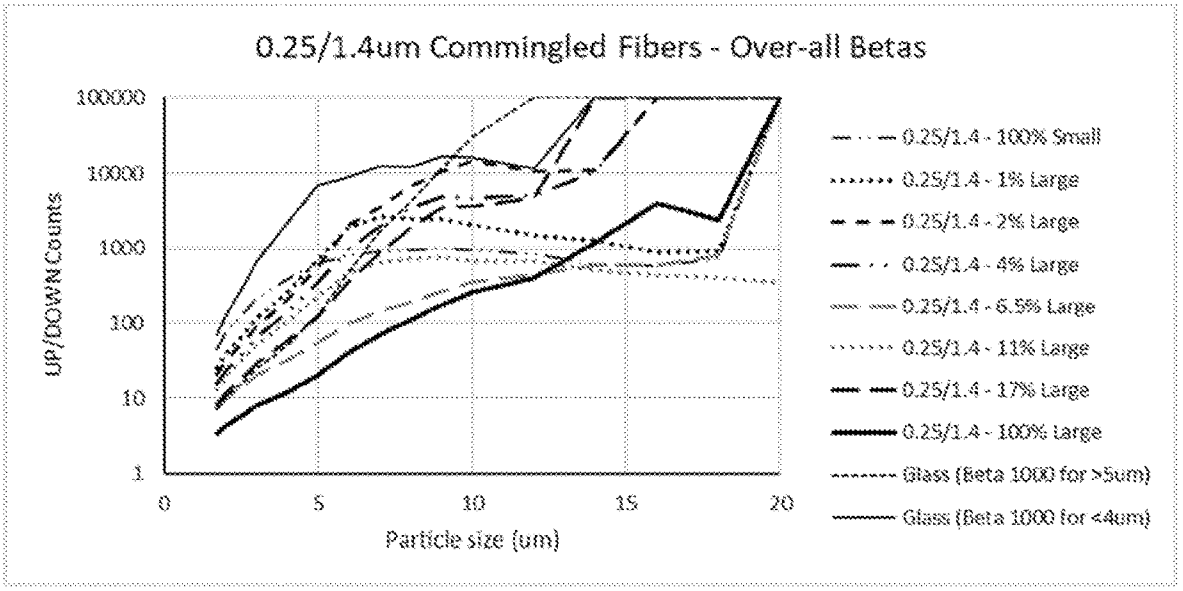

0.25/1.4um Layered Fibers - Over-all Betas
UP/DOWN Counts
1000
100
10
1
1.5
2
2.5
3
3.5
4
4.5
5
Particle size (um)
0.25/1.4 - 100% Small
0.25/1.4 - 1% Large
0.25/1.4 - 2% Large
0.25/1.4 - 4% Large
0.25/1.4 - 6.5% Large
0.25/1.4 - 11% Large
0.25/1.4 - 17% Large
0.25/1.4 - 100% Large
Glass (Beta 1000 for >Sum)
Glass (Beta 1000 for <4um)

FIG. 13G


0.25/1.4um Commingled Fibers - Over-all Betas
UP/DOWN Counts
100000
10000
1000
100
10
1
0
5
10
15
20
Particle size (um)
0.25/1.4 - 100% Small
0.25/1.4 - 1% Large
0.25/1.4 - 2% Large
0.25/1.4 - 4% Large
0.25/1.4 - 6.5% Large
0.25/1.4 - 11% Large
0.25/1.4 - 17% Large
0.25/1.4 - 100% Large
Glass (Beta 1000 for >5um)
Glass (Beta 1000 for <4um)

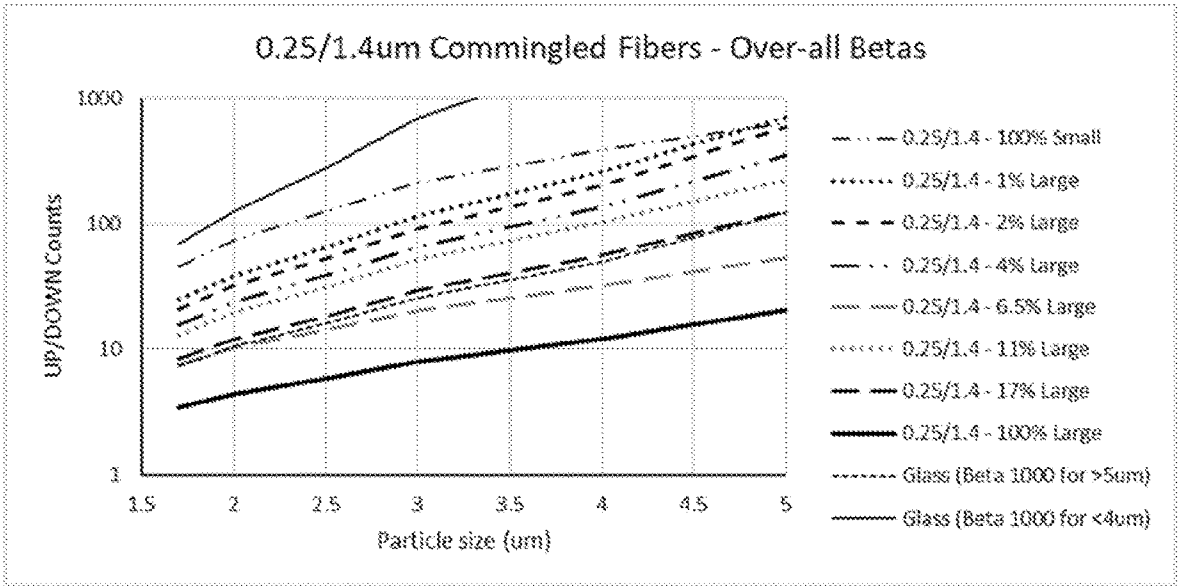

0.25/1.4um Commingled Fibers - Over-all Betas
UP/DOWN Counts
1000
100
10
1
1.5
2
2.5
3
3.5
4
4.5
5
Particle size (um)
0.25/1.4 - 100% Small
0.25/1.4 - 1% Large
0.25/1.4 - 2% Large
0.25/1.4 - 4% Large
0.25/1.4 - 6.5% Large
0.25/1.4 - 11% Large
0.25/1.4 - 17% Large
0.25/1.4 - 100% Large
Glass (Beta 1000 for >5um)
Glass (Beta 1000 for <4um)

FIG. 13H

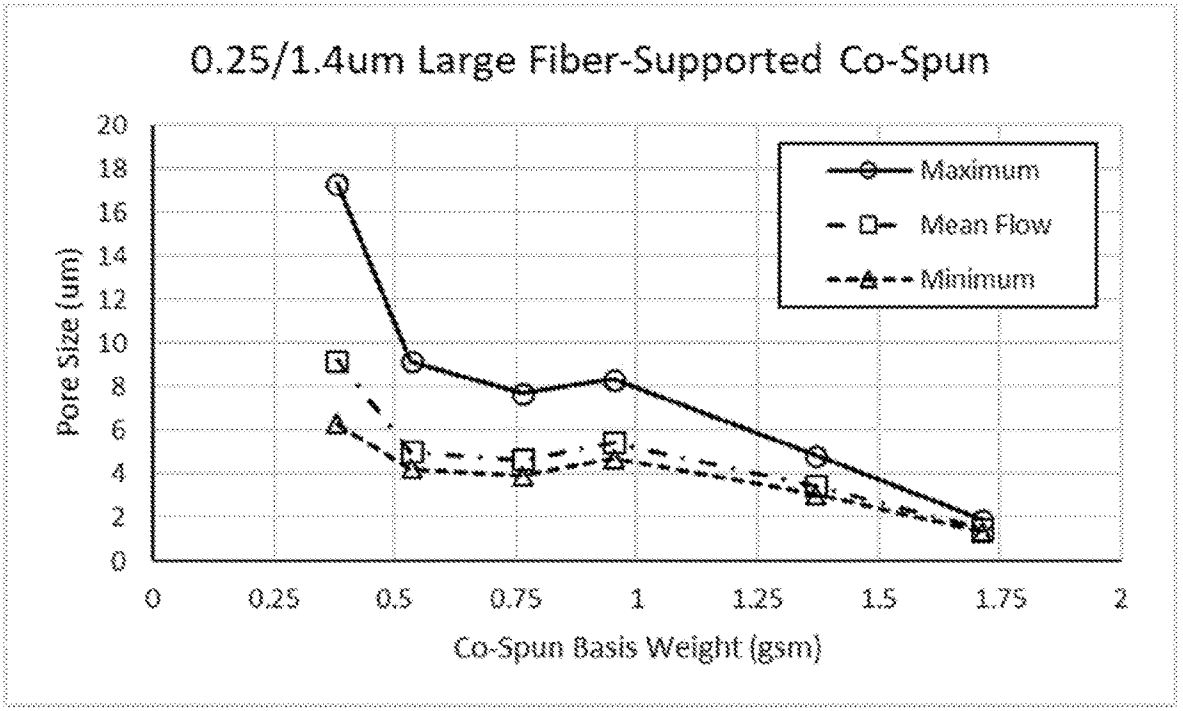
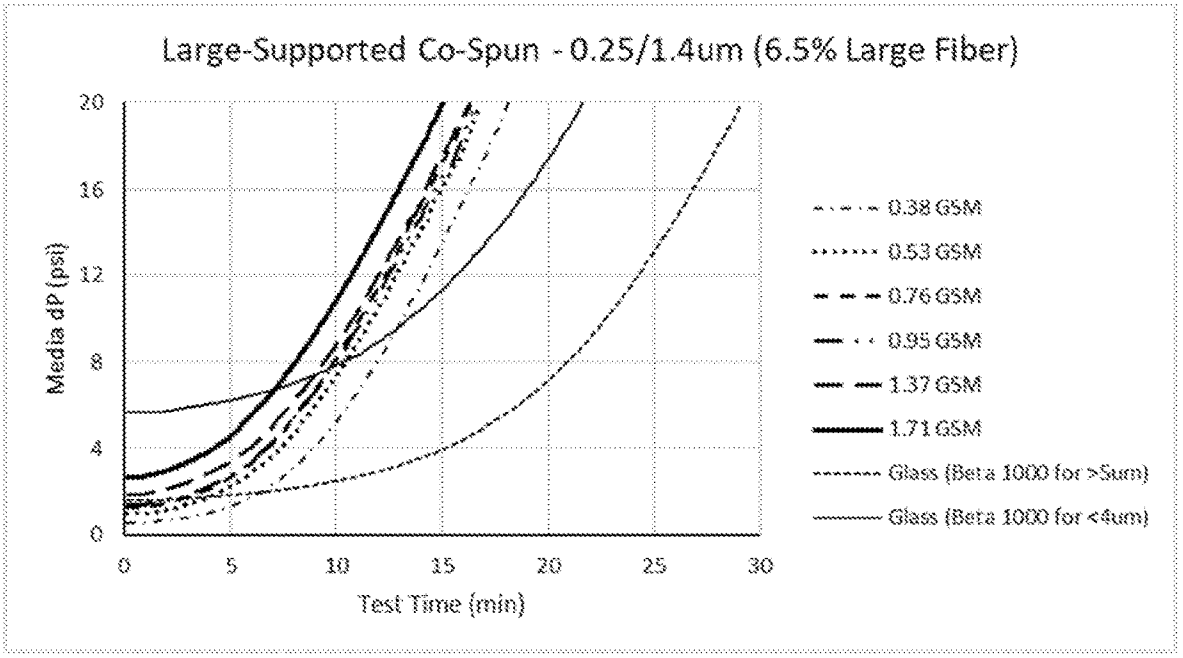

0.25/1.4um Large Fiber-Supported Co-Spun
Pore Size (um)
20
18
16
14
12
10
8
6
4
2
0
0
0.25
0.5
0.75
1
1.25
1.5
1.75
2
Co-Spun Basis Weight (gsm)
Maximum
Mean Flow
Minimum

FIG. 13I


Large-Supported Co-Spun - 0.25/1.4um (6.5% Large Fiber)
Media dP (psi)
20
16
12
8
4
0
0
5
10
15
20
25
30
Test Time (min)
0.38 GSM
0.53 GSM
0.76 GSM
0.95 GSM
1.37 GSM
1.71 GSM
Glass (Beta 1000 for >5um)
Glass (Beta 1000 for <4um)

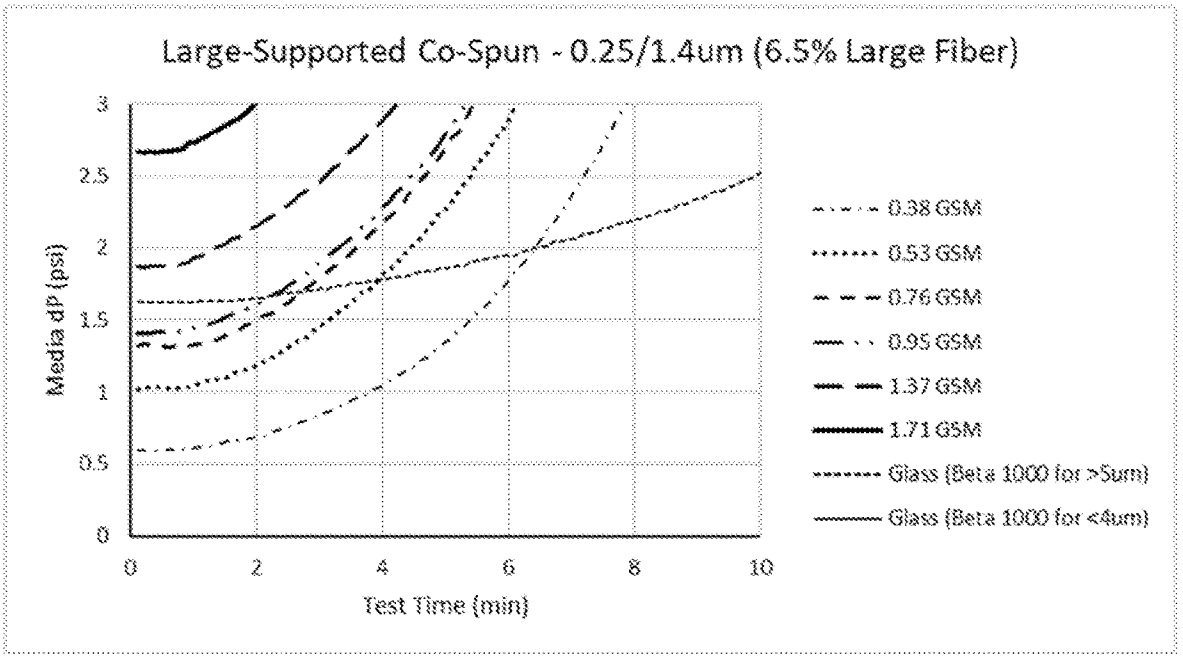
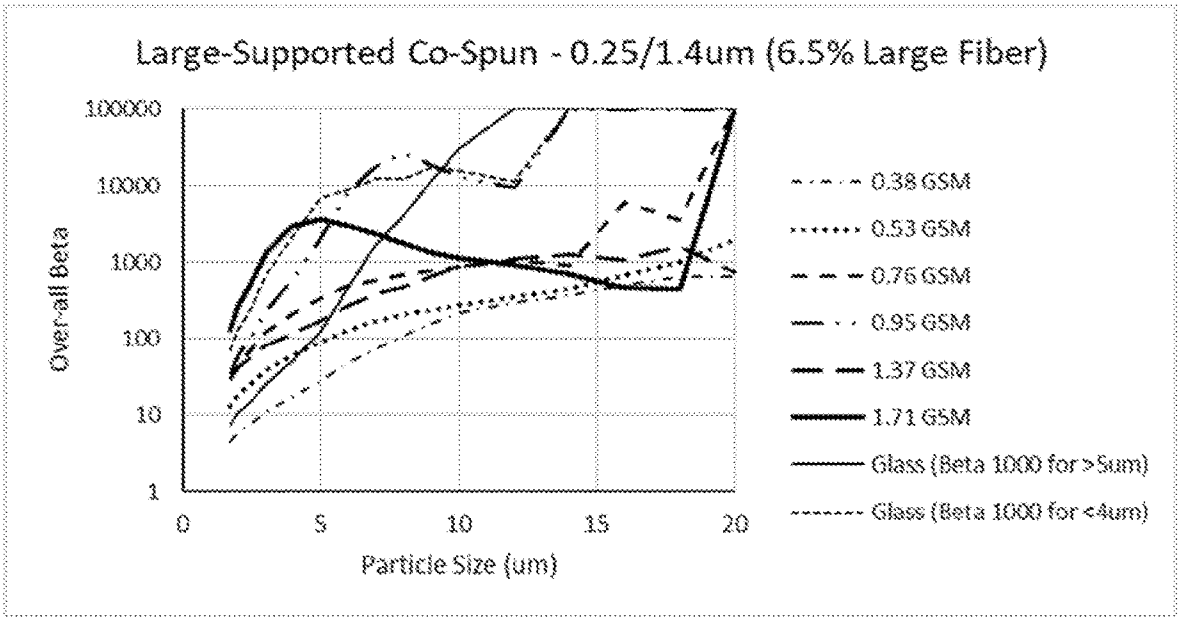

Large-Supported Co-Spun - 0.25/1.4um (6.5% Large Fiber)
Media dP (psi)
3
2.5
2
1.5
1
0.5
0
0
2
4
6
8
10
Test Time (min)
0.38 GSM
0.53 GSM
0.76 GSM
0.95 GSM
1.37 GSM
1.71 GSM
Glass (Beta 1000 for >5um)
Glass (Beta 1000 for <4um)

FIG. 13J


Large-Supported Co-Spun - 0.25/1.4um (6.5% Large Fiber)
Over-all Beta
100000
10000
1000
100
10
1
0
5
10
15
20
Particle Size (um)
0.38 GSM
0.53 GSM
0.76 GSM
0.95 GSM
1.37 GSM
1.71 GSM
Glass (Beta 1000 for >5um)
Glass (Beta 1000 for <4um)

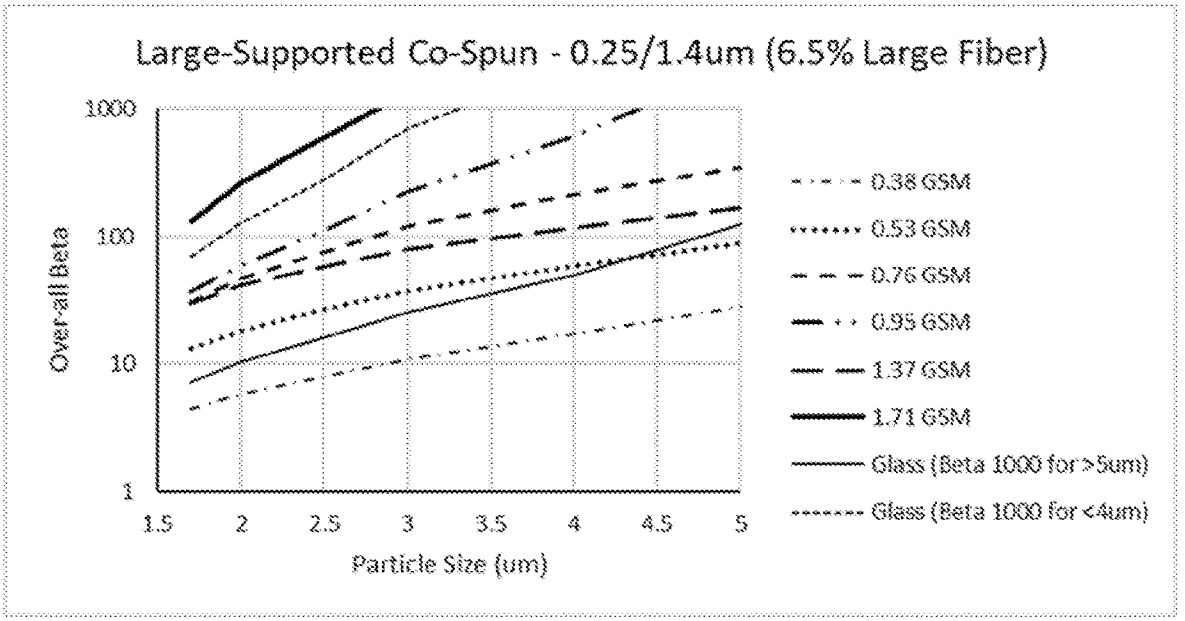

Large-Supported Co-Spun - 0.25/1.4um (6.5% Large Fiber)
Over-all Beta
1000
100
10
1
1.5
2
2.5
3
3.5
4
4.5
5
Particle Size (um)
0.38 GSM
0.53 GSM
0.76 GSM
0.95 GSM
1.37 GSM
1.71 GSM
Glass (Beta 1000 for >5um)
Glass (Beta 1000 for <4um)

FIG. 13K

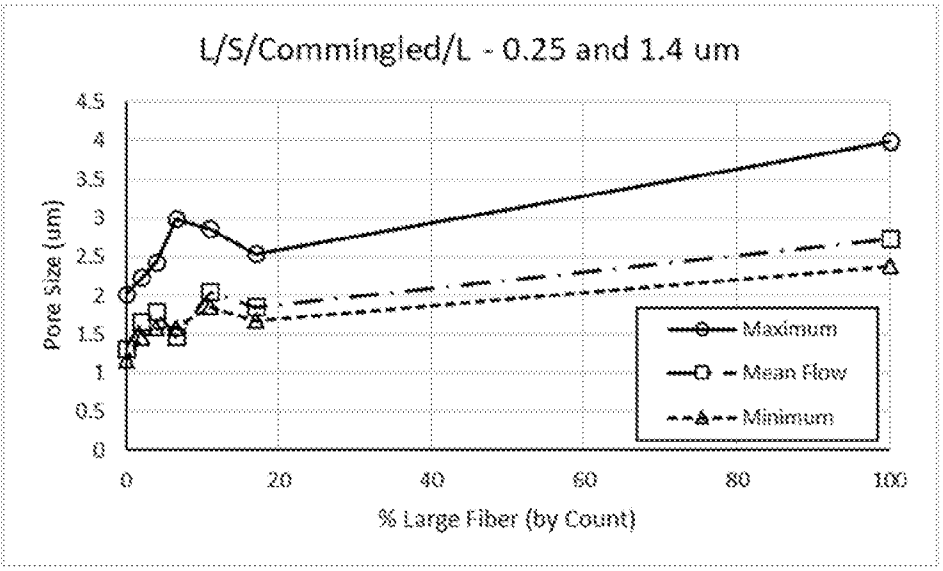

L/S/Commingled/L - 0.25 and 1.4 um
Pore Size (um)
4.5
4
3.5
3
2.5
2
1.5
1
0.5
0
0
20
40
60
80
100
% Large Fiber (by Count)
Maximum
Mean Flow
Minimum

FIG. 13L

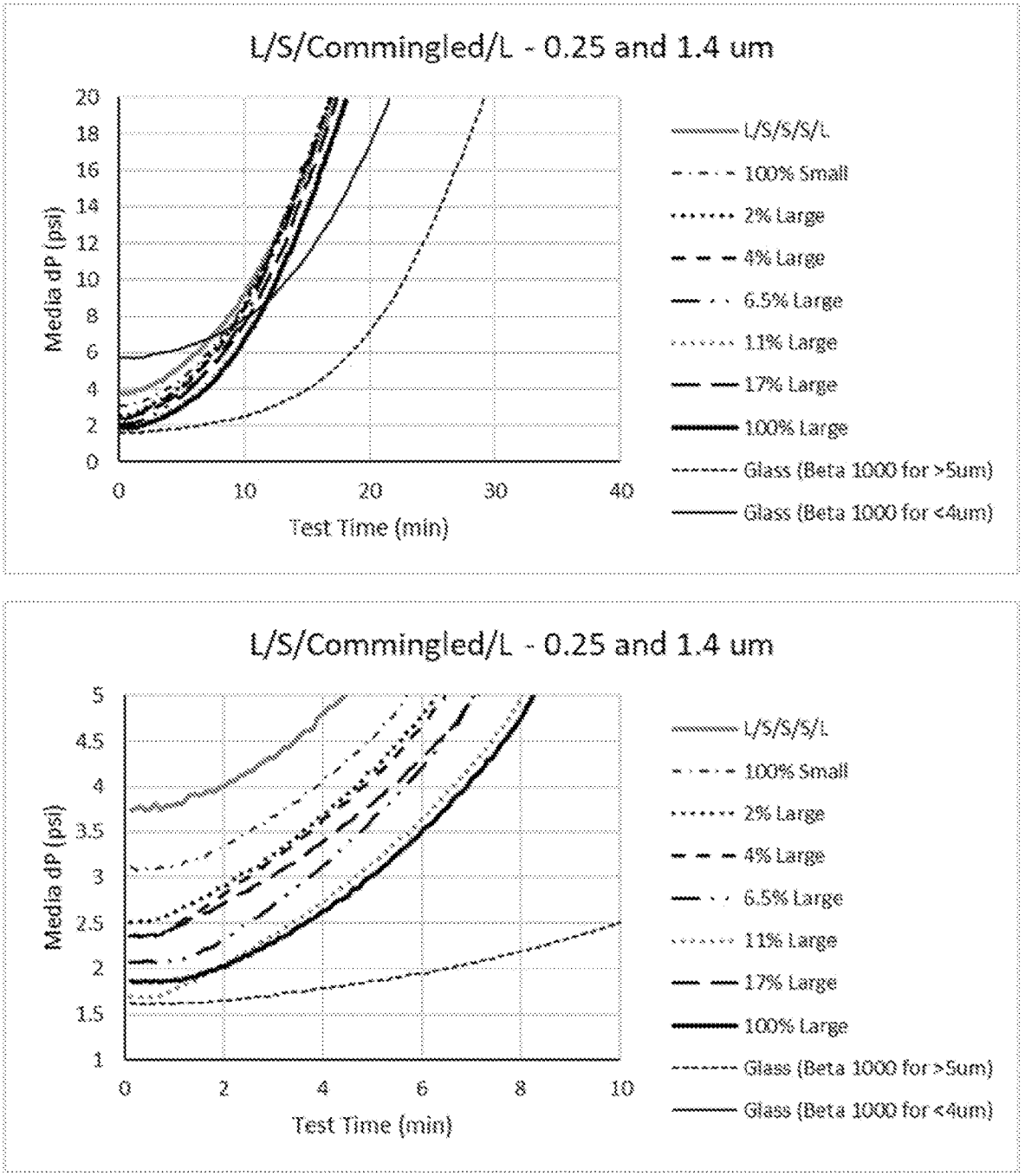
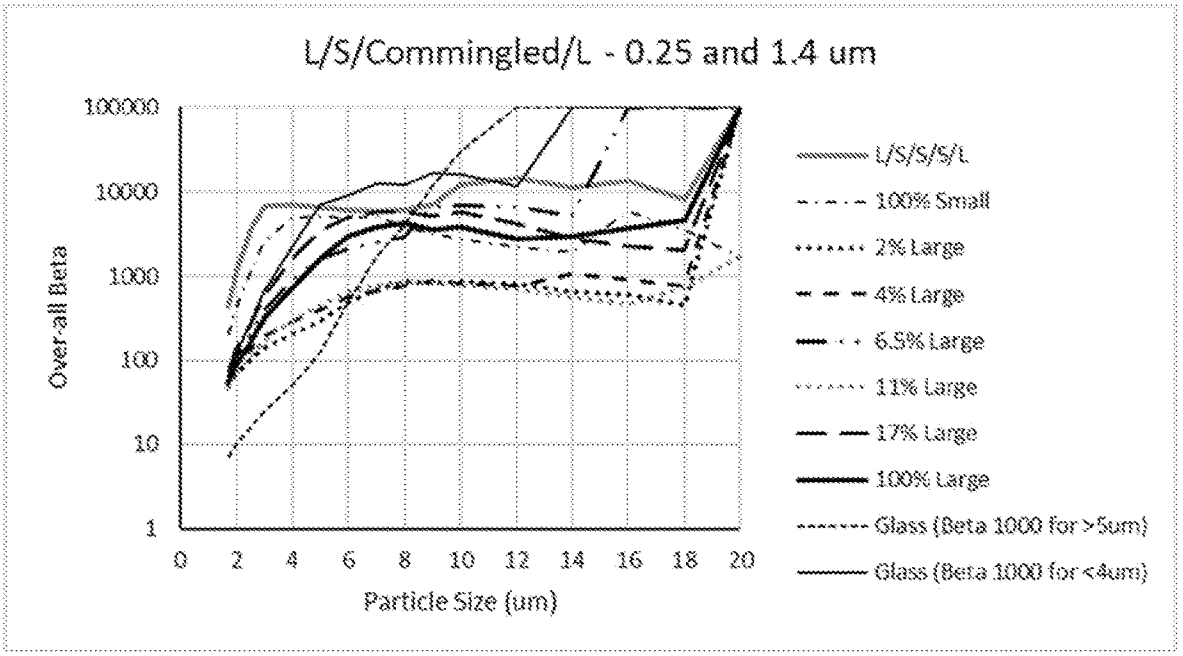

L/S/Commingled/L - 0.25 and 1.4 um
Media dP (psi)
Test Time (min)
L/S/S/S/L
100% Small
2% Large
4% Large
6.5% Large
11% Large
17% Large
100% Large
Glass (Beta 1000 for >5um)
Glass (Beta 1000 for <4um)
L/S/Commingled/L - 0.25 and 1.4 um
Media dP (psi)
Test Time (min)
L/S/S/S/L
100% Small
2% Large
4% Large
6.5% Large
11% Large
17% Large
100% Large
Glass (Beta 1000 for >5um)
Glass (Beta 1000 for <4um)

FIG. 13M


L/S/Commingled/L - 0.25 and 1.4 um
Over-all Beta
100000
10000
1000
100
10
1
0 2 4 6 8 10 12 14 16 18 20
Particle Size (um)
L/S/S/S/L
100% Small
2% Large
4% Large
6.5% Large
11% Large
17% Large
100% Large
Glass (Beta 1000 for >5um)
Glass (Beta 1000 for <4um)

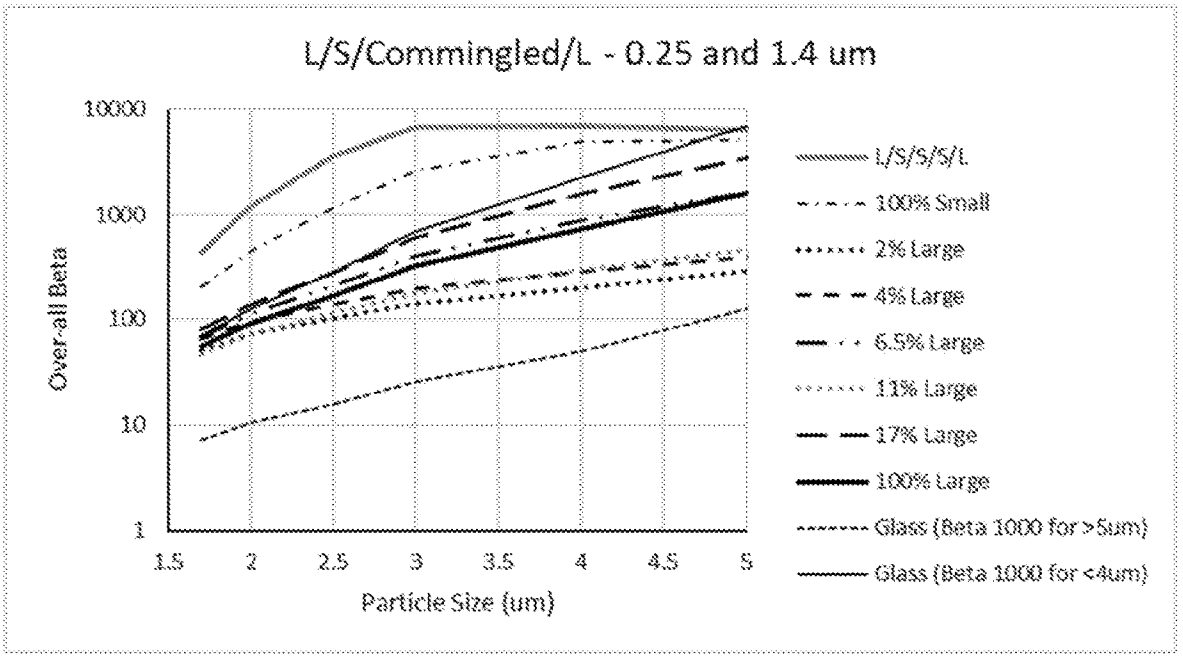

L/S/Commingled/L - 0.25 and 1.4 um
Over-all Beta
10000
1000
100
10
1
1.5 2 2.5 3 3.5 4 4.5 5
Particle Size (um)
L/S/S/S/L
100% Small
2% Large
4% Large
6.5% Large
11% Large
17% Large
100% Large
Glass (Beta 1000 for >5um)
Glass (Beta 1000 for <4um)

FIG. 14A

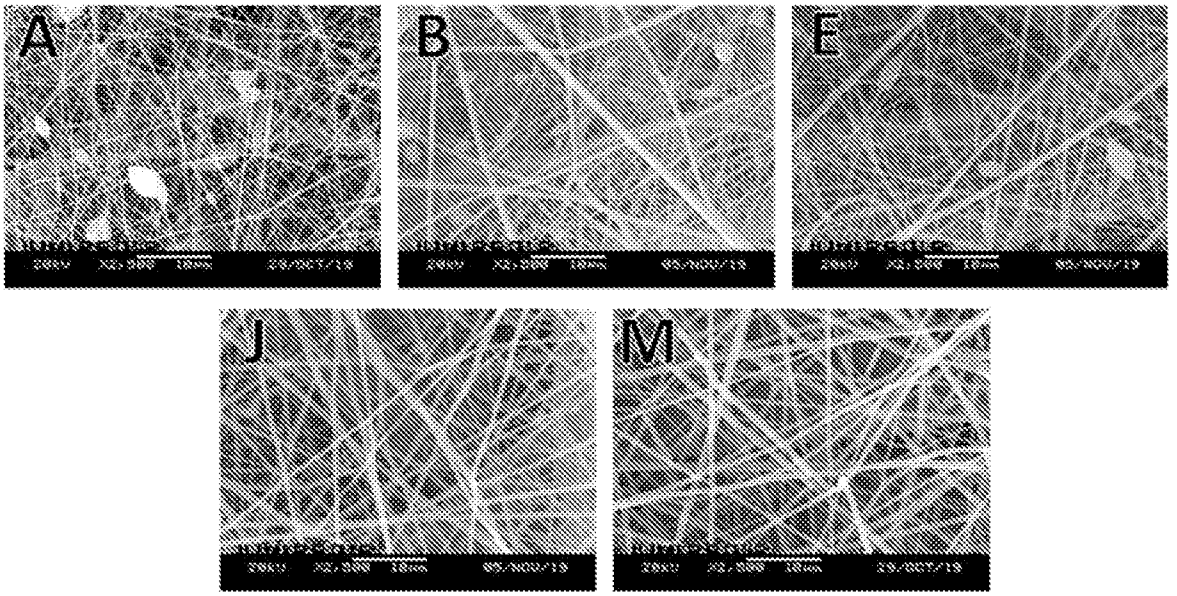



FIG. 14B

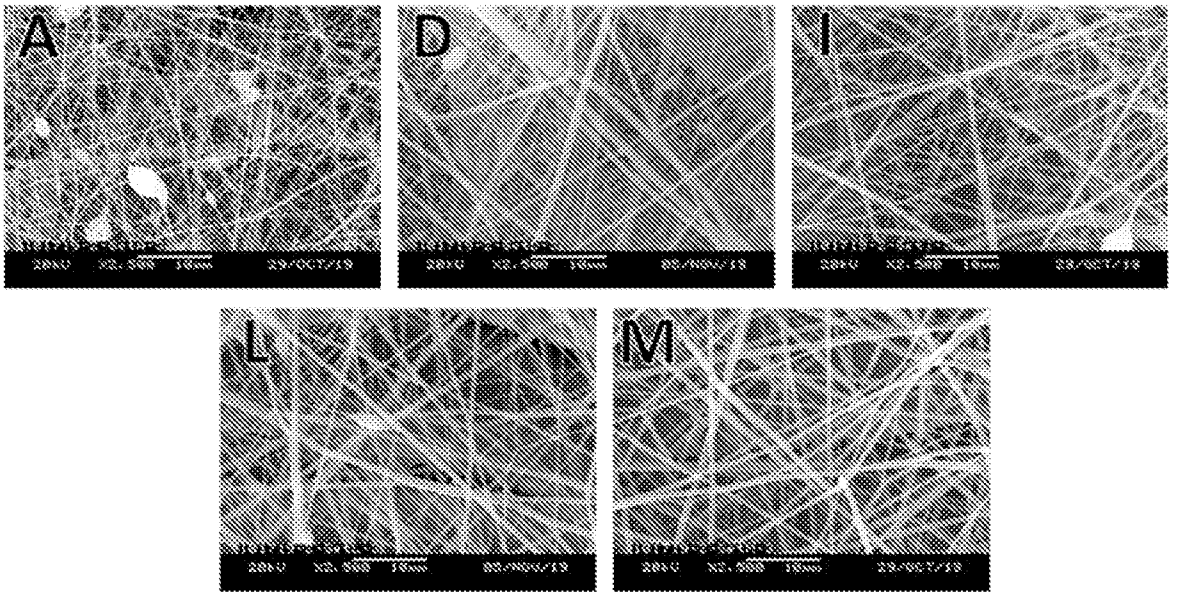


FIG. 14C

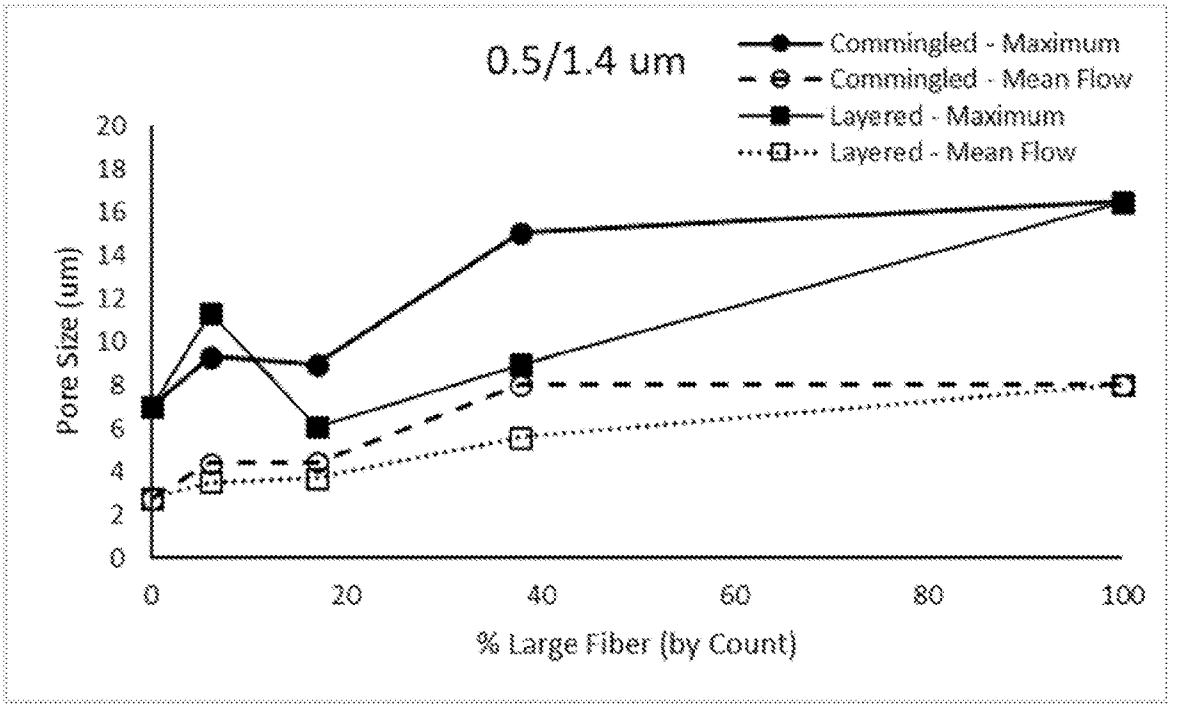



FIG. 14D

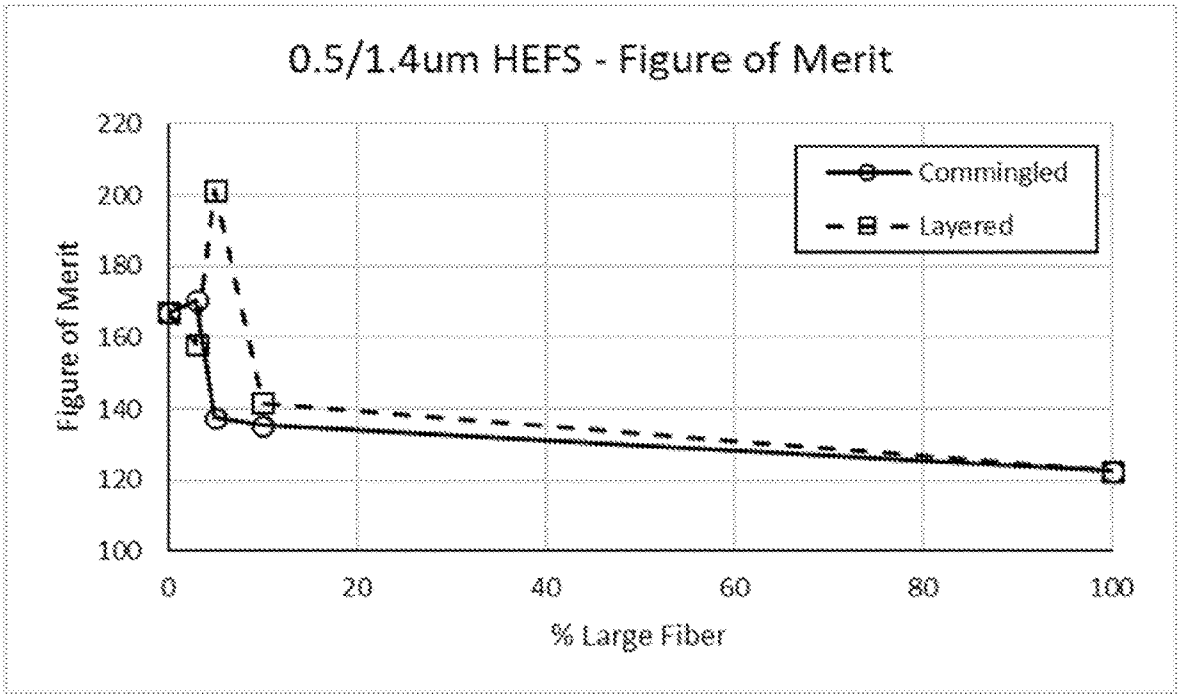
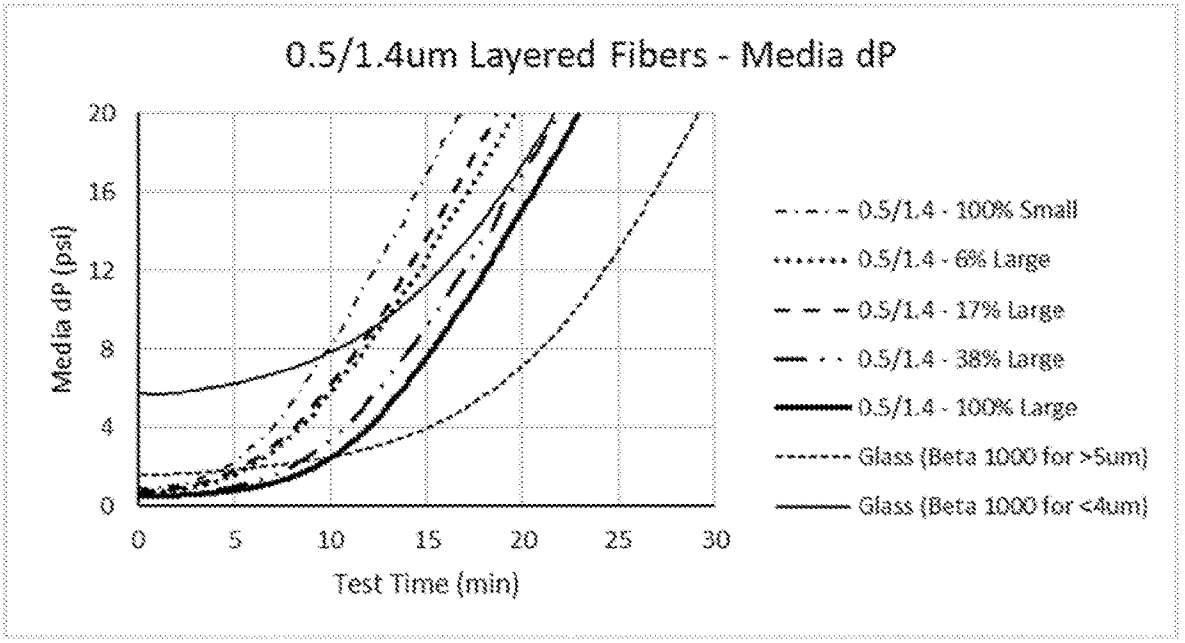


FIG. 14E


0.5/1.4um Layered Fibers - Media dP
Media dP (psi)
20
16
12
8
4
0
0
5
10
15
20
25
30
Test Time (min)
0.5/1.4 - 100% Small
0.5/1.4 - 6% Large
0.5/1.4 - 17% Large
0.5/1.4 - 38% Large
0.5/1.4 - 100% Large
Glass (Beta 1000 for >5um)
Glass (Beta 1000 for <4um)

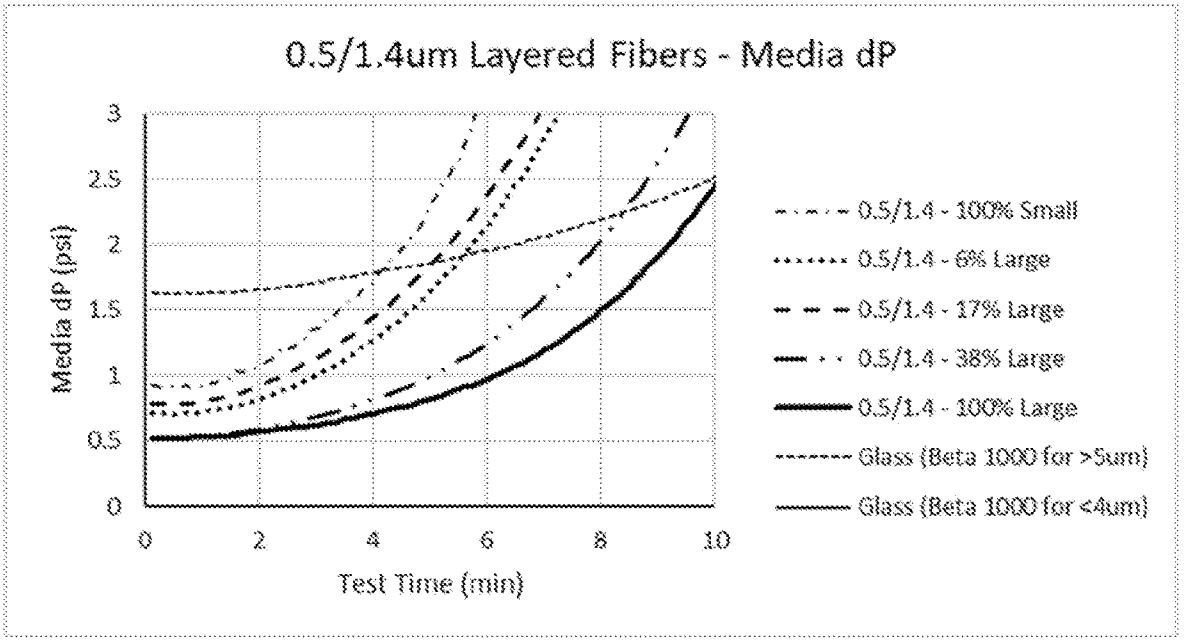
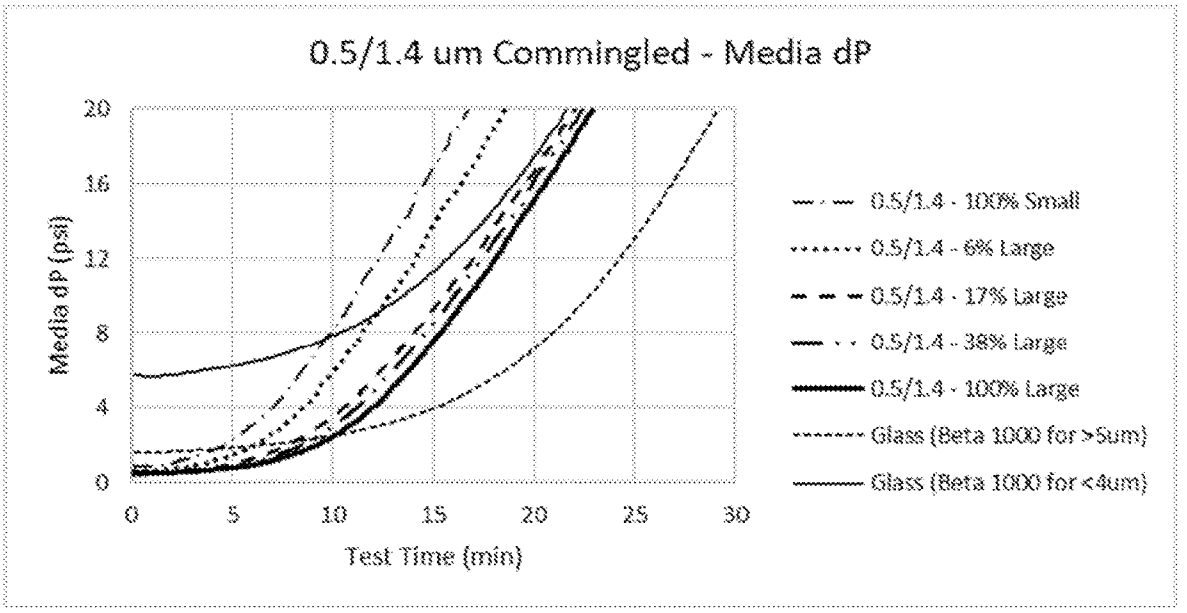

0.5/1.4um Layered Fibers - Media dP
Media dP (psi)
3
2.5
2
1.5
1
0.5
0
0
2
4
6
8
10
Test Time (min)
0.5/1.4 - 100% Small
0.5/1.4 - 6% Large
0.5/1.4 - 17% Large
0.5/1.4 - 38% Large
0.5/1.4 - 100% Large
Glass (Beta 1000 for >5um)
Glass (Beta 1000 for <4um)

FIG. 14F


0.5/1.4 um Commingled - Media dP
Media dP (psi)
20
16
12
8
4
0
0
5
10
15
20
25
30
Test Time (min)
0.5/1.4 - 100% Small
0.5/1.4 - 6% Large
0.5/1.4 - 17% Large
0.5/1.4 - 38% Large
0.5/1.4 - 100% Large
Glass (Beta 1000 for >5um)
Glass (Beta 1000 for <4um)

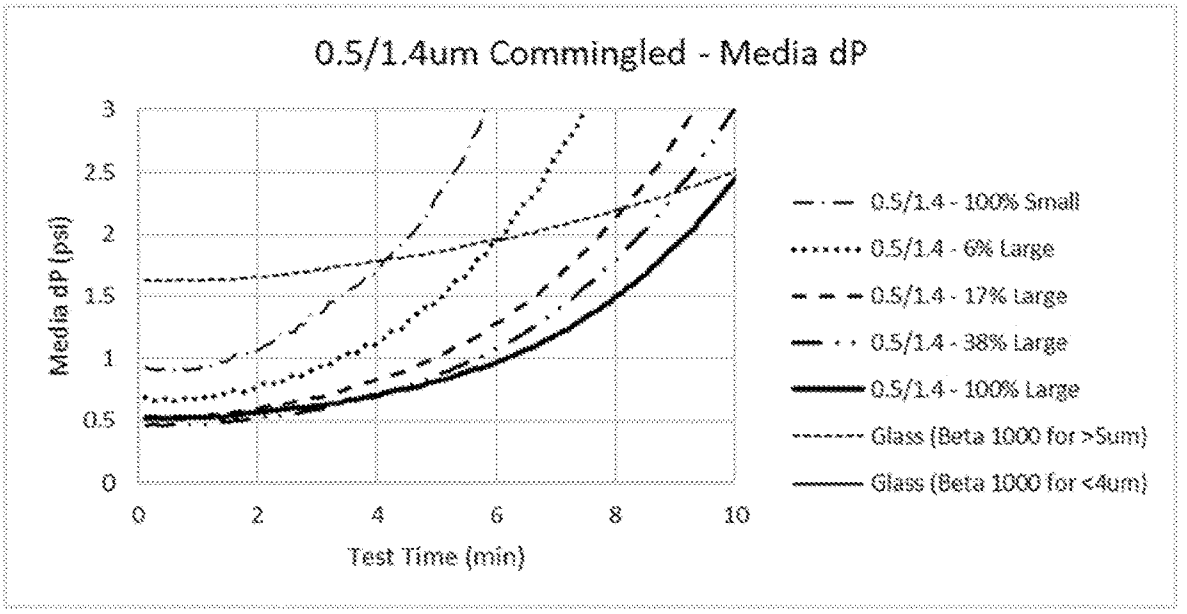
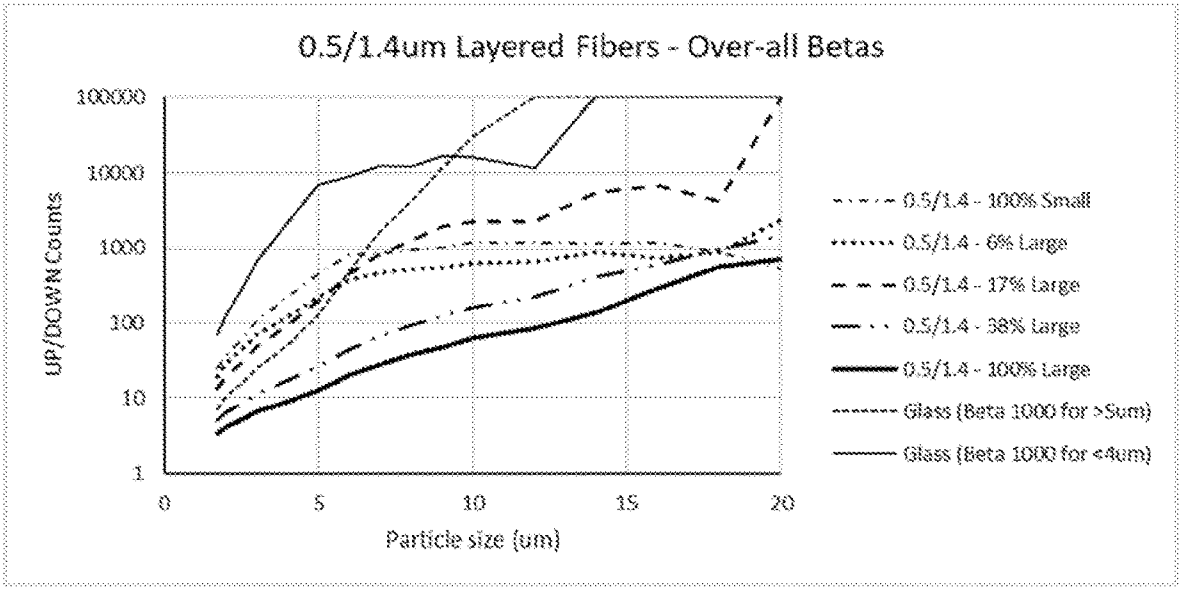

0.5/1.4um Commingled - Media dP
Media dP (psi)
3
2.5
2
1.5
1
0.5
0
0
2
4
6
8
10
Test Time (min)
0.5/1.4 - 100% Small
0.5/1.4 - 6% Large
0.5/1.4 - 17% Large
0.5/1.4 - 38% Large
0.5/1.4 - 100% Large
Glass (Beta 1000 for >5um)
Glass (Beta 1000 for <4um)

FIG. 14G


0.5/1.4um Layered Fibers - Over-all Betas
UP/DOWN Counts
100000
10000
1000
100
10
1
0
5
10
15
20
Particle size (um)
0.5/1.4 - 100% Small
0.5/1.4 - 6% Large
0.5/1.4 - 17% Large
0.5/1.4 - 38% Large
0.5/1.4 - 100% Large
Glass (Beta 1000 for >5um)
Glass (Beta 1000 for <4um)

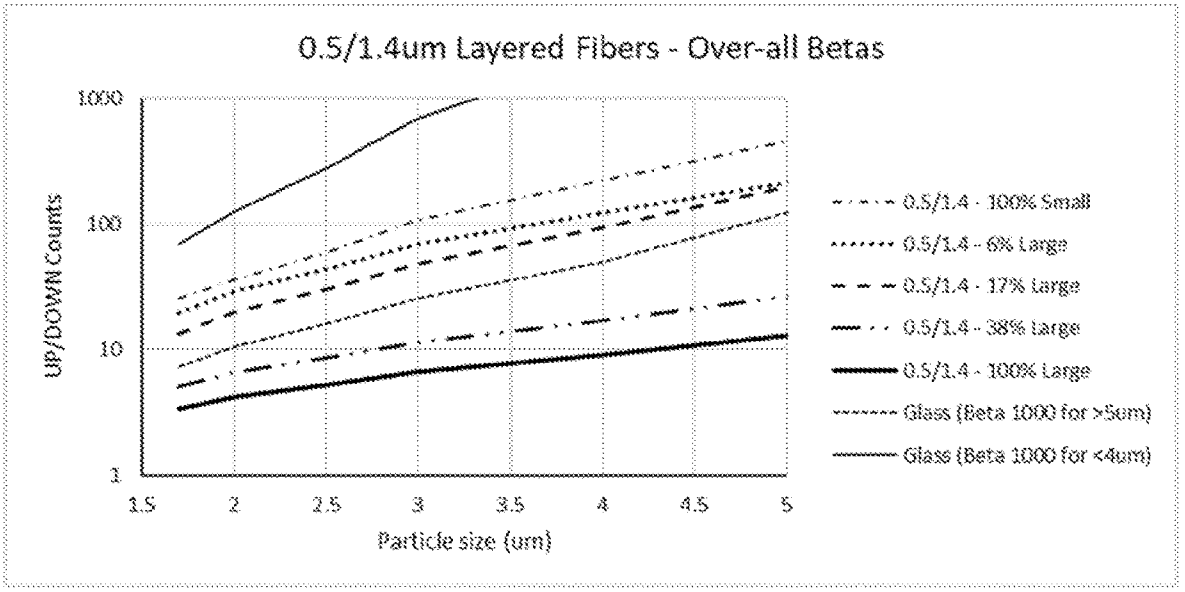
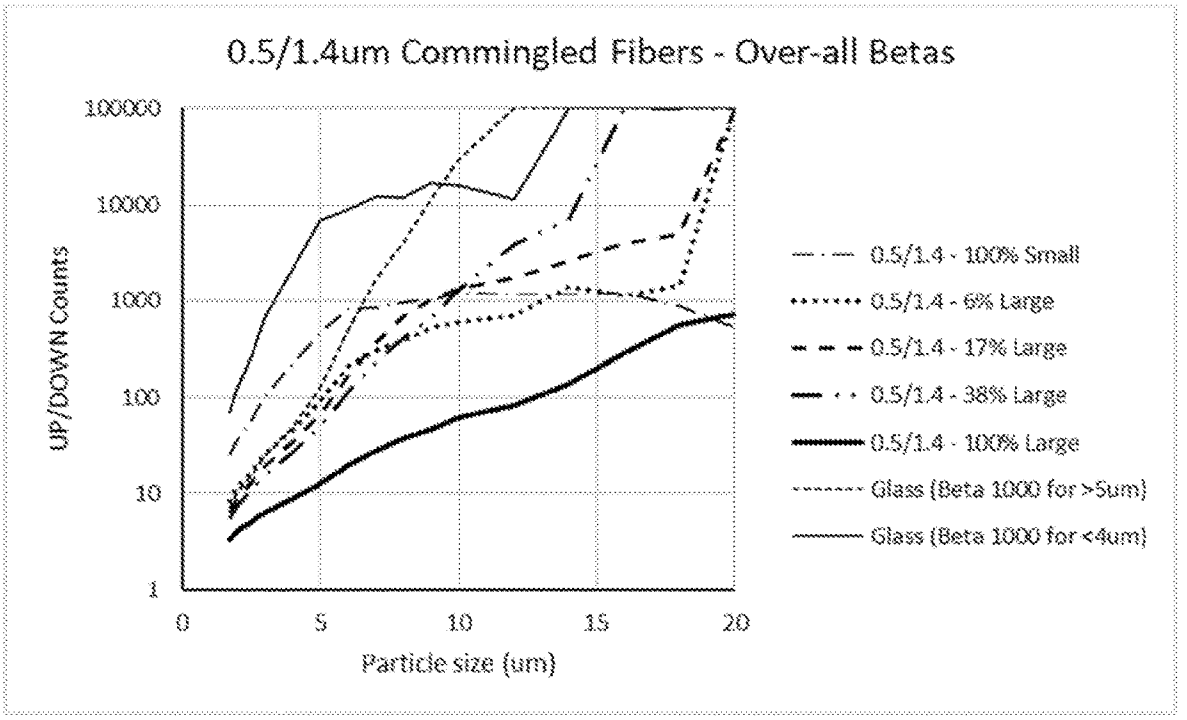

0.5/1.4um Layered Fibers - Over-all Betas
UP/DOWN Counts
1000
100
10
1
1.5
2
2.5
3
3.5
4
4.5
5
Particle size (um)
0.5/1.4 - 100% Small
0.5/1.4 - 6% Large
0.5/1.4 - 17% Large
0.5/1.4 - 38% Large
0.5/1.4 - 100% Large
Glass (Beta 1000 for >5um)
Glass (Beta 1000 for <4um)

FIG. 14H


0.5/1.4um Commingled Fibers - Over-all Betas
UP/DOWN Counts
100000
10000
1000
100
10
1
0
5
10
15
20
Particle size (um)
0.5/1.4 - 100% Small
0.5/1.4 - 6% Large
0.5/1.4 - 17% Large
0.5/1.4 - 38% Large
0.5/1.4 - 100% Large
Glass (Beta 1000 for >5um)
Glass (Beta 1000 for <4um)

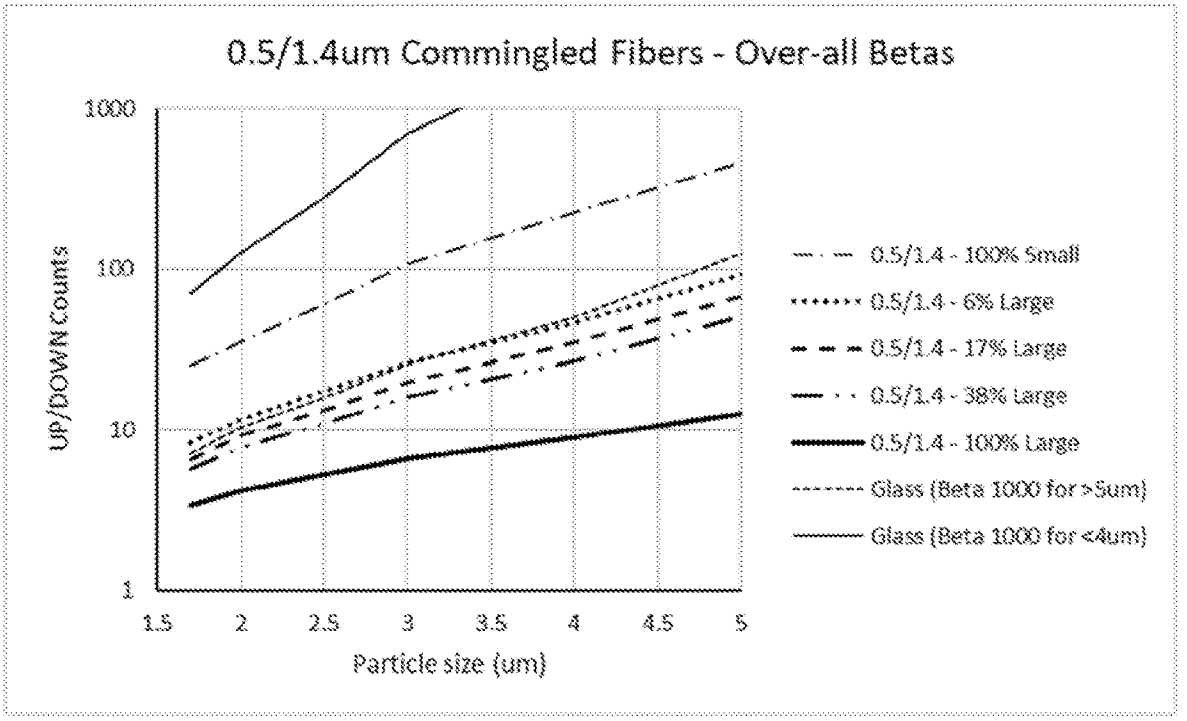

0.5/1.4um Commingled Fibers - Over-all Betas
UP/DOWN Counts
1000
100
10
1
1.5
2
2.5
3
3.5
4
4.5
5
Particle size (um)
0.5/1.4 - 100% Small
0.5/1.4 - 6% Large
0.5/1.4 - 17% Large
0.5/1.4 - 38% Large
0.5/1.4 - 100% Large
Glass (Beta 1000 for >5um)
Glass (Beta 1000 for <4um)

FIG. 14I

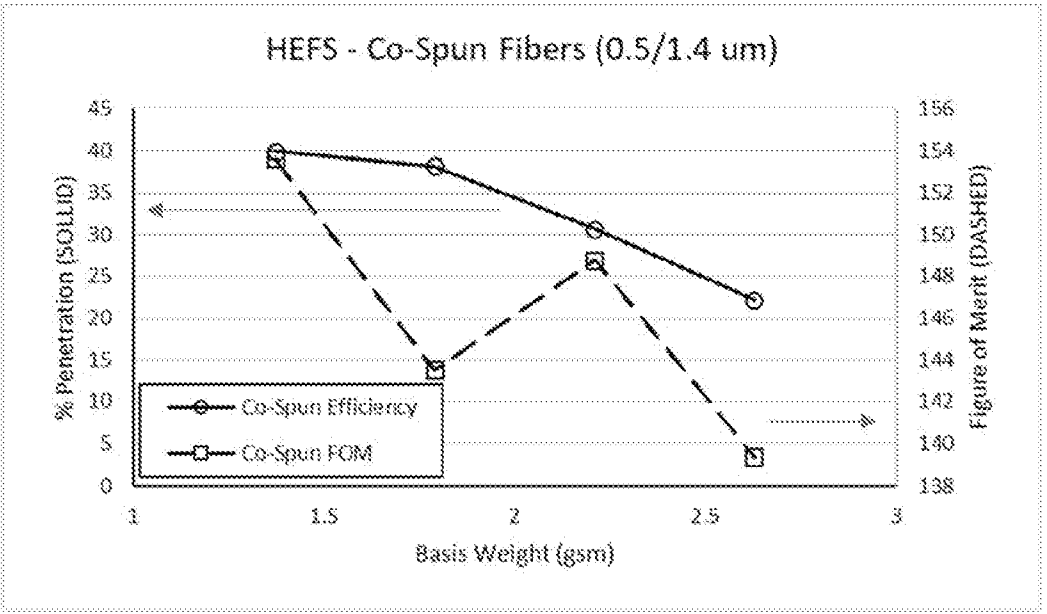

HEFS - Co-Spun Fibers (0.5/1.4 um)
% Penetration (SOLID)
Figure of Merit (DASHED)
Basis Weight (gsm)
Co-Spun Efficiency
Co-Spun FOM
45
40
35
30
25
20
15
10
5
0
156
154
152
150
148
146
144
142
140
138
1
1.5
2
2.5
3

FIG. 15A

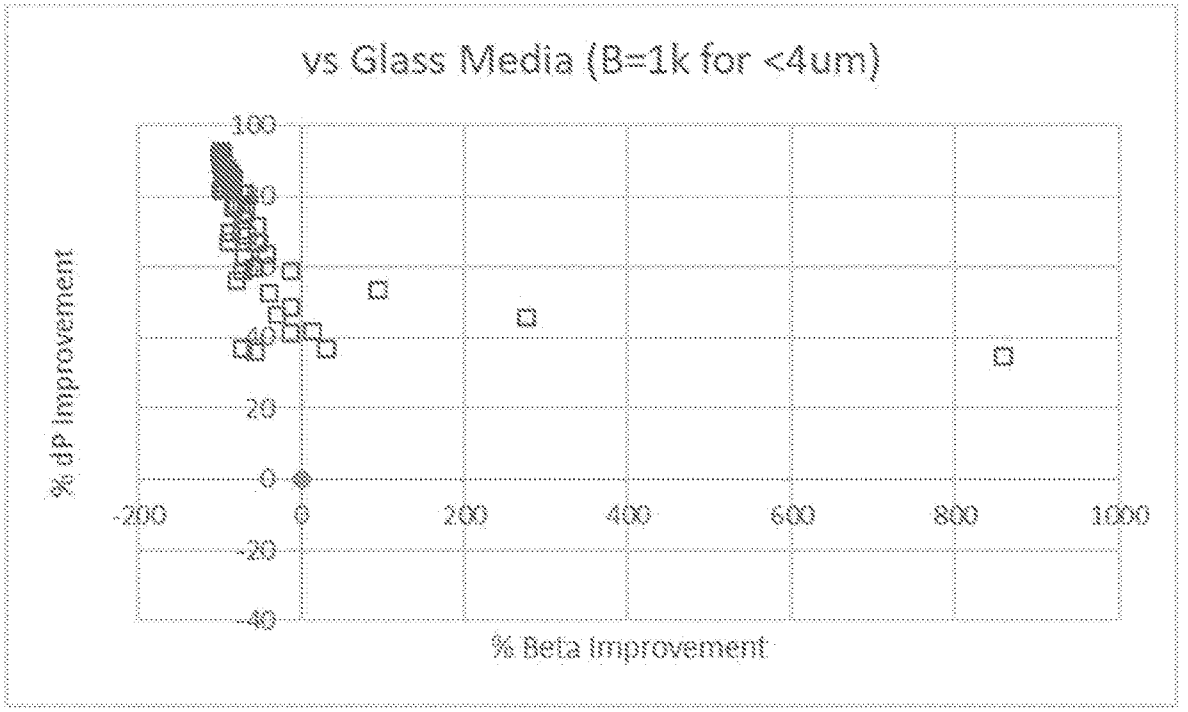



FIG. 15B

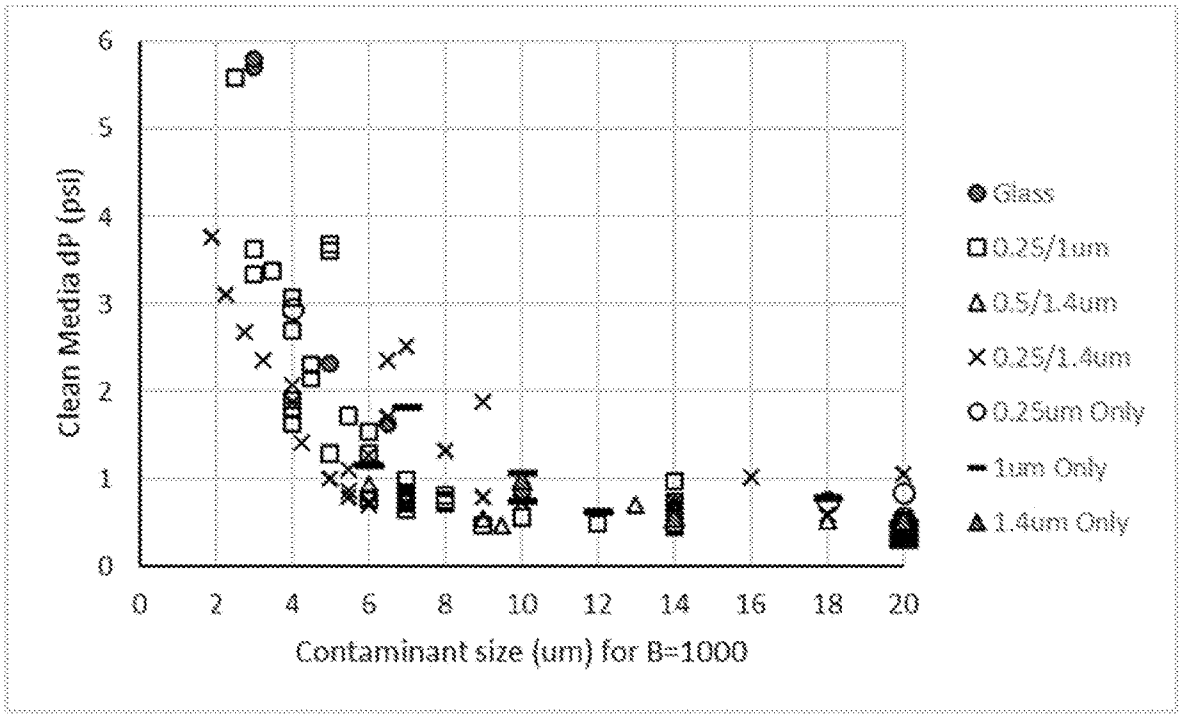


FIG. 16A

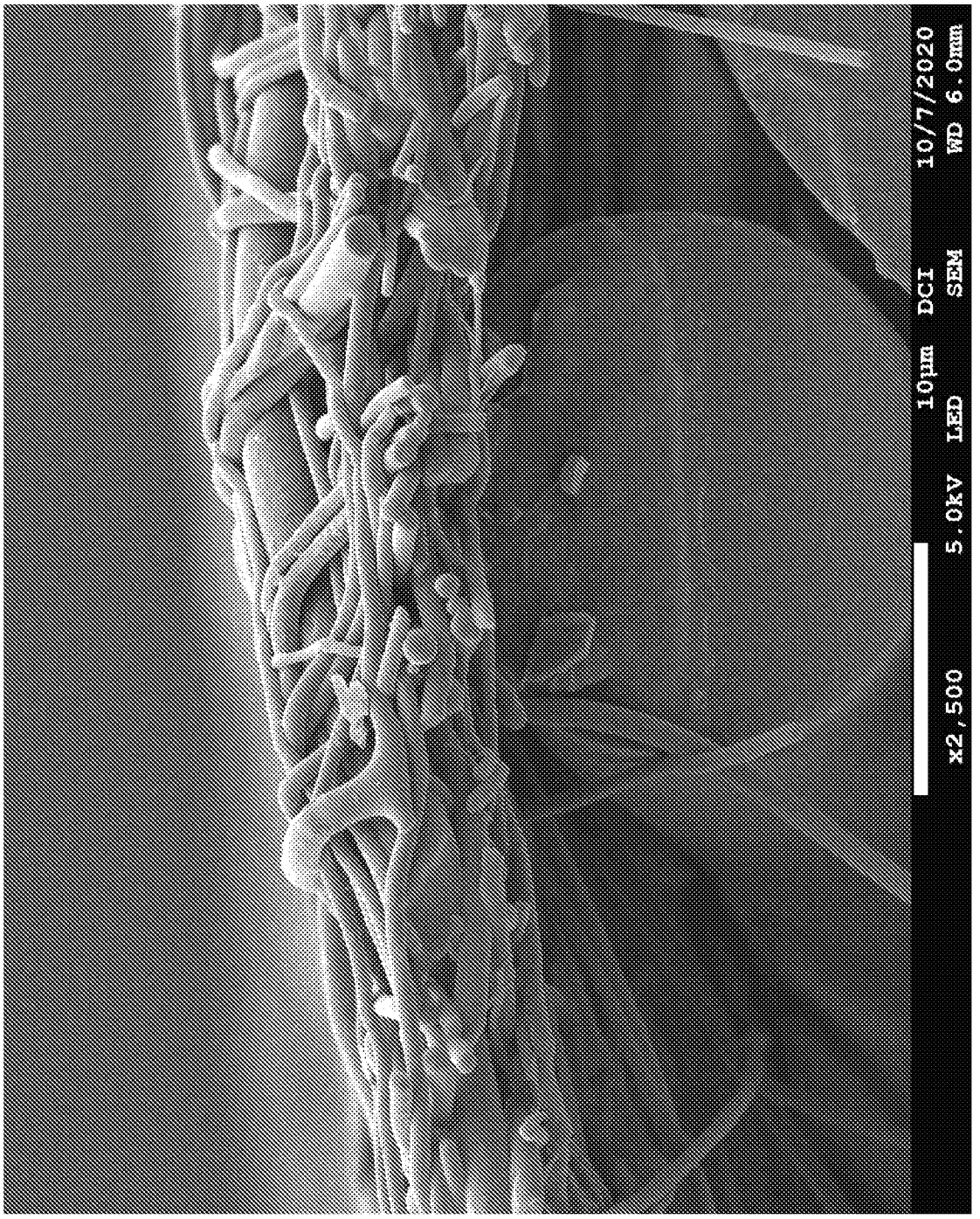


FIG. 16B

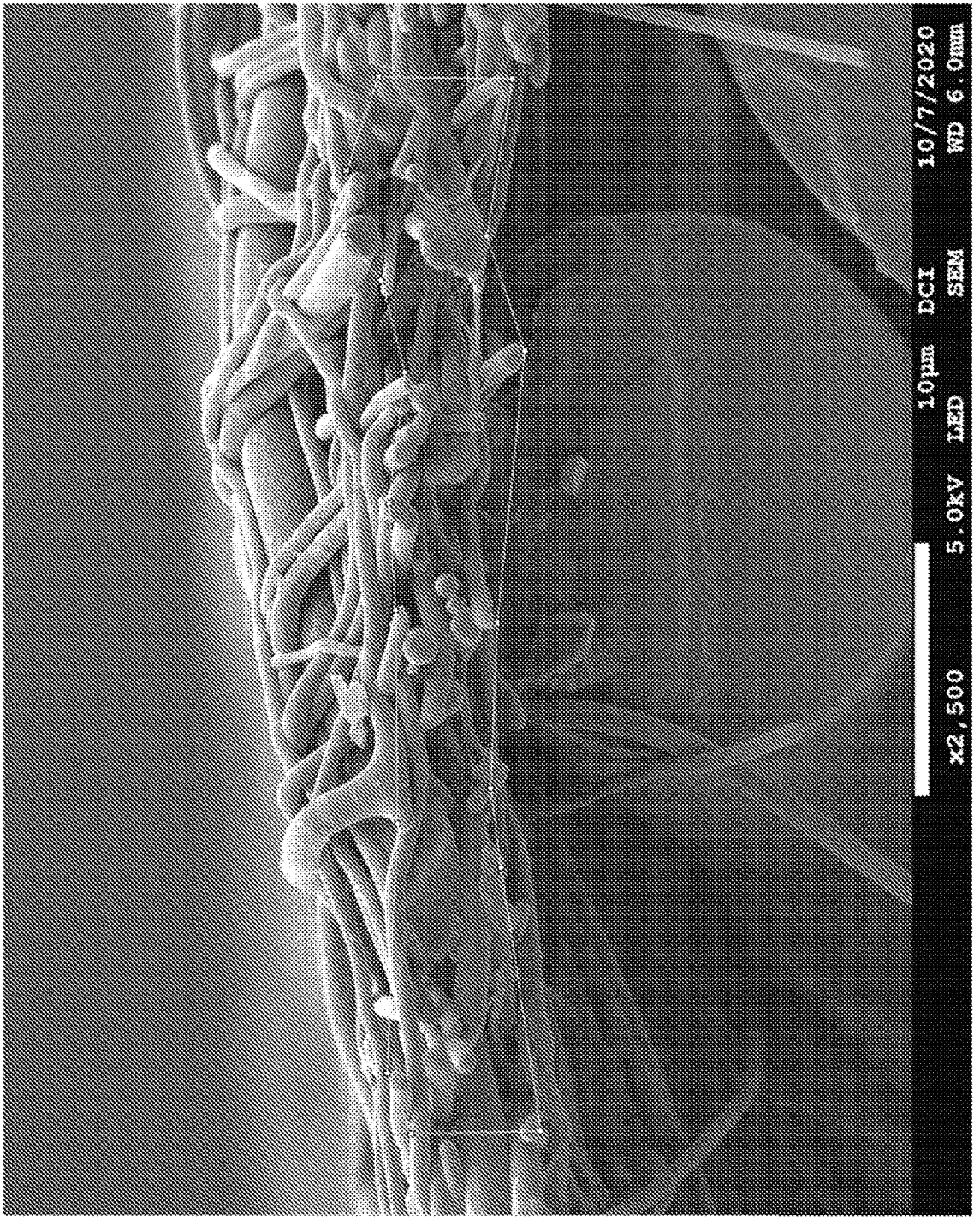


FIG. 16C

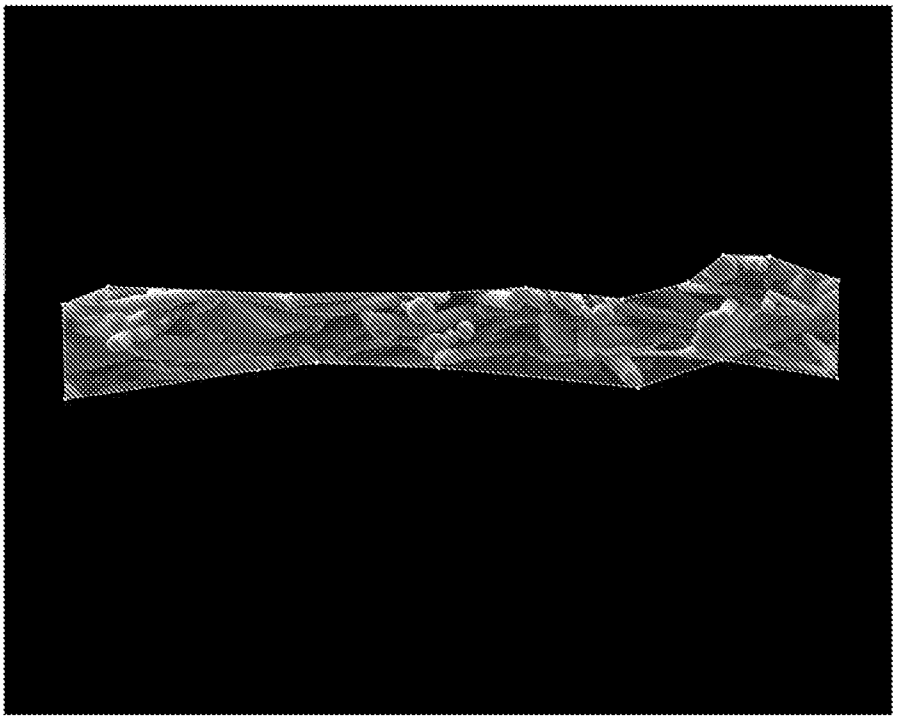
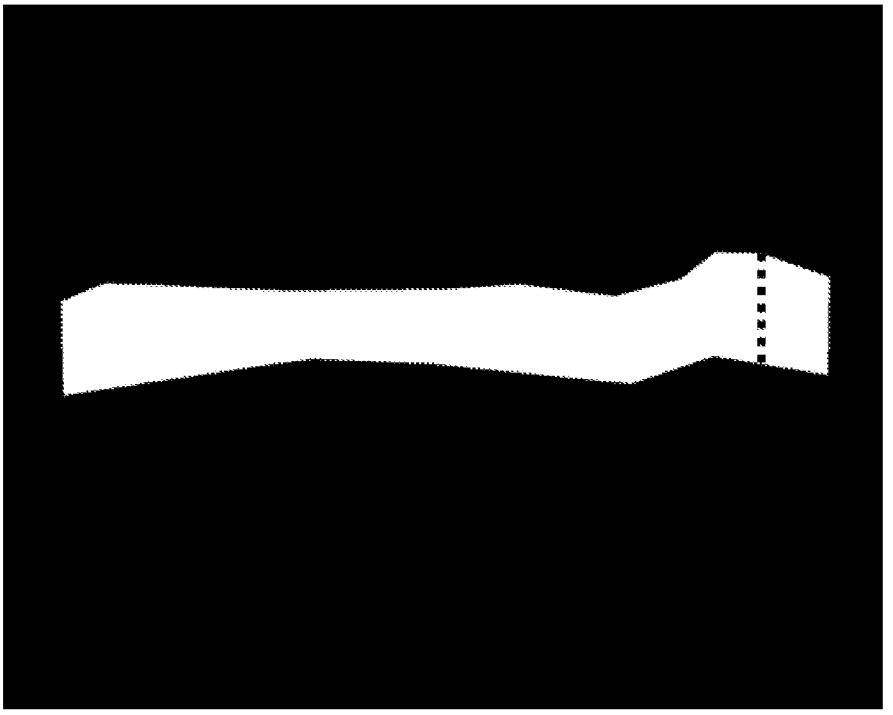


FIG. 16D



# FILTER MEDIA LAYERS INCLUDING MIXED DIAMETER FINE FIBERS

## CROSS-REFERENCE TO RELATED APPLICATIONS

**[0001]** This application claims the benefit of U.S. Provisional Application Ser. No. 62/912,456, filed 8 Oct. 2019; U.S. Provisional Application Ser. No. 62/947,998, filed 13 Dec. 2019; U.S. Provisional Application Ser. No. 62/952,979, filed 23 Dec. 2019; U.S. Provisional Application Ser. No. 62/992,003, filed 19 Mar. 2020; and U.S. Provisional Application Ser. No. 63/004,602, filed 3 Apr. 2020 the disclosures of which are incorporated by reference herein in their entireties.

## SUMMARY OF THE INVENTION

**[0002]** This disclosure describes a high performing (including, for example, high efficiency and low pressure drop) filtration media. In some embodiments, this disclosure describes filter media that achieves the efficiency of filter media that includes fine glass fibers without the inclusion of fine glass fibers.

**[0003]** In one aspect, this disclosure describes a filtration media that includes a support layer and a fine fiber layer. The fine fiber layer is deposited on the support layer, and the fine fiber layer includes large fine fibers and small fine fibers. The large fine fibers having an average diameter of at least 1 μm and are at least 3 times the average diameter of small fine fibers.

**[0004]** In some embodiments, the large fine fibers have a diameter at least 0.2 μm, at least 0.3 μm, or at least 0.4 μm greater than a diameter of the small fine fibers.

**[0005]** In some embodiments, the fine fiber layer includes a first layer of fine fibers, wherein the first layer of fine fibers includes the large fine fibers and the small fine fibers.

**[0006]** In some embodiments, the fine fiber layer includes a first layer of fine fibers and a second layer of fine fibers, wherein the first layer of fine fibers is deposited on the support layer, and the second layer of fine fibers is deposited on the first layer of fine fibers.

**[0007]** When the fine fiber layer includes a first layer of fine fibers and a second layer of fine fibers, in some embodiments, the first layer of fine fibers includes fibers having an average diameter at least 3 times the average fiber diameter of a fine fiber of the second layer of fine fibers.

**[0008]** In some embodiments, the second layer of fine fibers includes fibers of two different diameters. When the second layer of fine fibers includes fibers of two different diameters, the fibers of two different diameters may include small fine fibers and large fine fiber, wherein the large fine fibers having an average diameter at least 3 times the average diameter of the small fine fibers.

**[0009]** In some embodiments, the small fine fibers of the second layer of fine fibers are deposited on the first layer of fine fibers, and the large fine fibers of the second layer of fine fibers are deposited on the small fine fibers of the second layer of fine fibers.

**[0010]** In some embodiments, the small fine fibers of the second layer of fine fibers are commingled with the large fine fibers of the second layer of fine fibers.

**[0011]** In some embodiments, at least some of the fine fibers are prepared by a method that includes providing a fiber-forming polymer; providing a polymer-reactive resinous aldehyde composition, wherein the polymer-reactive resinous aldehyde composition is reactive with the fiber-forming polymer; and combining the fiber-forming polymer and reactive resinous aldehyde composition to form a plurality of fine fibers.

**[0012]** In some embodiments, at least some of the fine fibers are prepared by a method that includes providing a fiber-forming polymer, wherein the fiber-forming polymer comprises a nonreactive polymer, that is a polymer unable to crosslink with the polymer-non-reactive resinous aldehyde composition; providing a polymer-non-reactive resinous aldehyde composition, wherein the polymer-non-reactive resinous aldehyde composition comprises one or more reactive groups that are capable of self-crosslinking; and combining the fiber-forming polymer and reactive resinous aldehyde composition to form a plurality of fine fibers.

**[0013]** In some embodiments, at least some of the fine fibers are prepared by a method that includes providing at least one fiber-forming polymer; providing at least two reactive additives reactive with each other, and optionally reactive with the fiber-forming polymer; and combining the at least one fiber-forming polymer and the at least two reactive additives under conditions effective to form a plurality of fine fibers.

**[0014]** In some embodiments, the support layer includes a spunbond layer.

**[0015]** In some embodiments, the support layer and the fine fiber layer form a composite having a composite mean flow pore size, and wherein the composite mean flow pore size is up to 6 μm, up to 9 μm, or up to 11 μm.

**[0016]** In some embodiments, the fine fiber layer has a thickness of up to 5 μm, up to 10 μm, up to 30 μm, or up to 50 μm.

**[0017]** In some embodiments, the small fine fibers have an average diameter of at least 0.2 μm. In some embodiments, the small fine fibers have an average diameter of up to 0.3 μm, up to 0.4 μm, up to 0.5 μm, or up to 0.6 μm.

**[0018]** In some embodiments, the fine fibers are compatible with at least one of a hydraulic fluid, fuel, or lubricant.

**[0019]** In another aspect, this disclosure describes a filter element that includes a filtration media described herein. The filtration media form or may form or may form a part of an efficiency layer of the filter element. In some embodiments, the filter element further includes a loading layer.

**[0020]** As used herein, a "fiber" has an average fiber diameter of up to 100 micrometers. As used herein, fibers having an "average" diameter indicates that in a sample of a plurality of fibers, the average fiber diameter of that population of fibers in that sample has the indicated average fiber diameter. A population of fibers includes fibers having a diameter within 25% of an average fiber diameter. For example, a population of fibers having an average diameter of 1 μm includes fibers having a diameter of at least 750 nm and up to 1250 nm. In another example, a population of fibers having an average diameter of 250 nm includes fibers having a diameter of at least 188 nm and up to 313 nm. In a further example, a population of fibers having an average diameter of 500 nm includes fibers having a diameter of at least 375 nm and up to 625 nm. In yet another example, a population of fibers having an average diameter of 1400 nm includes fibers having a diameter of at least 1050 nm and up to 1750 nm. Fiber diameter may be measured using a top-down SEM image. The sample may be sputter-coated. A useful sputter-coater may be a gold and palladium mixture

including, for example, a Au:Pd 60:40 mixture. A more accurate fiber diameter measurement may be obtained by measuring the diameter of the fiber in at least 30 locations in the sample. Software such as a Trainable Weka Segmentation (an ImageJ plug-in) may be useful for analyzing fiber diameters.

**[0021]** As used herein, "fine fiber" refers to a fiber having a diameter of up to 10 micrometers (μm). In some embodiments, the fine fiber has a diameter of at least 50 nm or at least 0.1 μm.

**[0022]** The term "diameter" with respect to fibers refers either to the diameter of a circular cross-section of a fiber, or to a largest cross-sectional dimension of a non-circular cross-section of a fiber.

**[0023]** The term "particle size," as used herein, is refers to a particle's diameter, determined as described in ISO 11171: 2016.

**[0024]** As used herein, "commingled" fibers or a "commingled fiber structure" refer to fibers having at least two different diameters, wherein fibers having an average first diameter and fibers having an average second diameter are commingled, that is, wherein a fiber or mixed within the same layer of a media structure as a result of the fibers having been formed or deposited simultaneously or by using very short (for example, up to 10 seconds, up to 20 seconds, or up to 30 seconds) pulses of each polymer solution. When visualized using a top-down SEM image, fibers having an average first diameter may be observed as being located both below and above fibers having an average second diameter.

**[0025]** As used herein, "layered" fibers or a "layered fiber structure" refer to fibers having at least two different diameters, wherein fibers having an average first diameter are not substantially entangled with the fibers having an average second diameter as a result of fibers of differing diameters having been alternately applied to a substrate.

**[0026]** As used herein, unless indicated otherwise, pore size (for example, average mean flow pore size or average maximum pore size) is determined using capillary flow porometry. Capillary flow porometry may be performed using a continuous pressure scan mode. An exemplary range of applied pressures that may be used is 0.0256 bar to 1.275 bar. It may be useful to use a wetting liquid having a surface tension of 16 dynes/cm and a contact angle of 0, including, for example Porofil Wetting Solution (Quantachrome Instruments, Anton Paar, Boynton Beach, Fla.). The sample may initially be tested wet, varying low pressure to high pressure, and then tested dry, again varying low pressure to high pressure. The test is typically performed at ambient temperature conditions (for example, 20° C. to 25° C.). 256 data points may be collected across the range of the scan of the pressures for both the dry curve and the wet curve. Typically, no tortuosity factor and/or a shape factor will be used (that is, for comparison to other test methods that use an adjustment factor, a factor equal to 1 may be used). An average pore size (for example, average mean flow pore size or average maximum pore size) may be calculated from the mean of at least three measurements (taken from at least three different sample locations. Individual measurements of maximum pore size may be detected at the bubble point, where the bubble point is found after fluid begins passing through the sample, and three consecutive measurement increase by at least 1%, where 256 data points are collected across the scan at a rate of approximately 17 data points per minute. The bubble point is the value at the start of this sequence of three points. Individual measurements of mean flow pore size may be calculated by determining the pressure where the wet curve and the "half-dry" curve cross. The half-dry curve is obtained by the mathematical division by 2 of $V'_{dry}$, where $V'_{dry}$ is the air flow through a dry sample as a function of diameter.

**[0027]** As used herein, the "β ratio" or "β" is the ratio of upstream particles to downstream particles. The more efficient the filter, the higher the β ratio. The β ratio is defined as follows:

$$B_d = \frac{N_{d,U}}{N_{d,D}}$$

where $N_{d,U}$ is the upstream particle count per unit fluid volume for particles of diameter d or greater and $N_{d,D}$ is the downstream particle count per unit fluid volume for particles of diameter d or greater. If present, the subscript attached to β indicates the particle size for which the ratio is being reported.

**[0028]** As used herein, "over-all β ratio" or "over-all (3" is the ratio of the sum of all upstream particles over the course of the assay to the sum of all downstream particles over the course of the assay:

$$\text{Over-all } \beta_d = \frac{\Sigma N_{d,U}}{\Sigma N_{d,D}}$$

where $N_{d,U}$ is the upstream particle count per unit fluid volume for particles of diameter d or greater and $N_{d,D}$ is the downstream particle count per unit fluid volume for particles of diameter d or greater. If present, the subscript attached to β indicates the particle size for which the ratio is being reported.

**[0029]** As used herein, "filtration efficiency" or "efficiency" refers to the percentage of the contaminant removed by the filter, calculated as follows:

$$e_d = 100\left(1 - \frac{1}{\beta_d}\right) \quad \text{(i)}$$

where e is the filtration efficiency and β is defined as indicated above. Thus, the efficiencies referred to herein are cumulative efficiencies. If present, the subscript attached to e indicates the particle size for which the ratio is being reported.

**[0030]** As used herein, "pressure drop" (also referred to herein as "dP" or "ΔP") relates to the pressure (exerted by a pump) necessary to force fluid through the filter or filter medium (prior to the addition of a contaminant) for a particular fluid velocity. Unless otherwise indicated, pressure drop is measured as described in ISO 3968:2017.

**[0031]** The words "preferred" and "preferably" refer to embodiments of the invention that may afford certain benefits, under certain circumstances. However, other embodiments may also be preferred, under the same or other circumstances. Furthermore, the recitation of one or more preferred embodiments does not imply that other embodiments are not useful and is not intended to exclude other embodiments from the scope of the invention.

**[0032]** The terms "comprises" and variations thereof do not have a limiting meaning where these terms appear in the description and claims. Such terms will be understood to imply the inclusion of a stated step or element or group of steps or elements but not the exclusion of any other step or element or group of steps or elements. By "consisting of" is meant including, and limited to, whatever follows the phrase "consisting of" Thus, the phrase "consisting of" indicates that the listed elements are required or mandatory, and that no other elements may be present. By "consisting essentially of" is meant including any elements listed after the phrase, and limited to other elements that do not interfere with or contribute to the activity or action specified in the disclosure for the listed elements. Thus, the phrase "consisting essentially of" indicates that the listed elements are required or mandatory, but that other elements are optional and may or may not be present depending upon whether they materially affect the activity or action of the listed elements.

**[0033]** As used herein, the phrase "substantially free of" means that the element listed after the phrase is not present in an amount that would interfere with or contribute to the activity or action specified in the disclosure for the listed elements. For example, a media that is "substantially free of" glass would not include glass in sufficient amount to contribute to the efficiency of the filter media.

**[0034]** Unless otherwise specified, "a," "an," "the," and "at least one" are used interchangeably and mean one or more than one.

**[0035]** Also herein, the recitations of numerical ranges by endpoints include all numbers subsumed within that range (for example, 1 to 5 includes 1, 1.5, 2, 2.75, 3, 3.80, 4, 5, etc.).

**[0036]** Herein, "up to" a number (for example, up to 50) includes the number (for example, 50).

**[0037]** For any method disclosed herein that includes discrete steps, the steps may be conducted in any feasible order. And, as appropriate, any combination of two or more steps may be conducted simultaneously.

**[0038]** All headings are for the convenience of the reader and should not be used to limit the meaning of the text that follows the heading, unless so specified.

**[0039]** Reference throughout this specification to "one embodiment," "an embodiment," "certain embodiments," or "some embodiments," etc., means that a particular feature, configuration, composition, or characteristic described in connection with the embodiment is included in at least one embodiment of the disclosure. Thus, the appearances of such phrases in various places throughout this specification are not necessarily referring to the same embodiment of the disclosure. Furthermore, the features, configurations, compositions, or characteristics may be combined in any suitable manner in one or more embodiments.

**[0040]** Any reference to standard methods (e.g., ASTM, TAPPI, AATCC, etc.) refer to the most recent available version of the method at the time of filing of this disclosure unless otherwise indicated.

**[0041]** Unless otherwise indicated, all numbers expressing quantities of components, molecular weights, and so forth used in the specification and claims are to be understood as being modified in all instances by the term "about." As used herein in connection with a measured quantity, the term "about" refers to that variation in the measured quantity as would be expected by the skilled artisan making the measurement and exercising a level of care commensurate with the objective of the measurement and the precision of the measuring equipment used. Accordingly, unless otherwise indicated to the contrary, the numerical parameters set forth in the specification and claims are approximations that may vary depending upon the desired properties sought to be obtained by the present invention. At the very least, and not as an attempt to limit the doctrine of equivalents to the scope of the claims, each numerical parameter should at least be construed in light of the number of reported significant digits and by applying ordinary rounding techniques.

**[0042]** Notwithstanding that the numerical ranges and parameters setting forth the broad scope of the invention are approximations, the numerical values set forth in the specific examples are reported as precisely as possible. All numerical values, however, inherently contain a range necessarily resulting from the standard deviation found in their respective testing measurements.

**[0043]** The above summary of the present invention is not intended to describe each disclosed embodiment or every implementation of the present invention. The description that follows more particularly exemplifies illustrative embodiments. In several places throughout the application, guidance is provided through lists of examples, which examples can be used in various combinations. In each instance, the recited list serves only as a representative group and should not be interpreted as an exclusive list.

## BRIEF DESCRIPTION OF THE FIGURES

**[0044]** FIG. **1**A shows β values versus time elapsed (in minutes) for samples prepared and tested as described in Example 1 (small fine fibers laid directly on scrim). FIG. **1**B shows exemplary SEM images (1000× magnification) of samples prepared as described in Example 1 (small fine fibers laid directly on scrim) and tested on a FHAST bench. FIG. **1**C shows β values versus time elapsed (in minutes) for samples prepared as described in Example 1 (small fine fibers overlaid on large fine fibers, large fine fibers laid direction on scrim). FIG. **1**D shows exemplary SEM images (1000× magnification) of samples prepared as described in Example 1 (small fine fibers overlaid on large fine fibers) and tested on a FHAST bench. FIG. **1**E shows an exemplary SEM image of a large fine fiber layer deposited on a nylon scrim (prior to small fine fibers being deposited on the large fine fiber layer) at 500× magnification (top panel) and 2000× magnification (bottom panel). In FIG. **1**A-FIG. **1**E, the "large" fine fibers have a fiber diameter at least 3 times the average fiber diameter of the "small" fine fiber. FIG. **1**F shows a schematic for a sample prepared as described in Example 1 (small fine fibers laid directly on scrim). FIG. **1**G shows a schematic for a sample prepared as described in Example 1 (small fine fibers overlaid on large fine fibers, large fine fibers laid direction on scrim). FIG. **1**H-FIG. **1**M show schematics of exemplary media constructions. In each construction, the support media is not shown but typically would be located on the downstream side of the media.

**[0045]** FIG. **2**A shows exemplary SEM images (1000× magnification) of samples prepared as described in Example 2 using Solution 1 to achieve small fine fibers (left panel), Solution 1 and Solution 2 to achieve commingled fine fibers of mixed (small and large) diameters (center panel), and Solution 2 to achieve large fine fibers (right panel). FIG. **2**B shows dP increase during test progression, for media made and tested as described in Example 2. FIG. **2**C shows

over-all β values for various dust particle sizes for bare scrim or media made and tested as described in Example 2.

**[0046]** FIG. **3**A shows exemplary SEM images (1000× magnification) of samples prepared as described in Example 3 according to Pendant Drop Sample Preparation Method 2 for a duration of 2 minutes using Solution 1 to achieve small fine fibers (left panel), Solution 1 and Solution 2 to achieve commingled fibers of mixed (small and large) diameters (center panel), or Solution 2 to achieve large fine fibers (right panel). FIG. **3**B-FIG. **3**C show an exemplary SEM image of a sample produced using Method 2 for a duration of 5 minutes (FIG. **3**B) or 1 minute (FIG. **3**C) of co-spinning Solution 1 and Solution 2 to achieve commingled fibers of mixed (small and large) diameters. The commingling of the fibers within the network is indicated by the presence of a single small fine fiber which is present both above and below large fine fibers. FIG. **3**D-FIG. **3**E show a comparison of media dP increase during test progression for media including small fine fibers, commingled fibers of mixed diameters, or large fine fibers (FIG. **3**D) media and media including commingled fibers of mixed diameters with varying basis weights (FIG. **3**E).

**[0047]** FIG. **3**F-FIG. **3**G show a comparison of over-all β values for a range of dust particle sizes for media including small fine fibers alone, media including commingled fibers of mixed diameters, or media including large fine fibers alone (FIG. **3**F) and media including commingled fibers of mixed diameters with varying basis weights (FIG. **3**G). FIG. **3**H shows the dependence of average maximum pore size (top panel) and average mean flow pore size (bottom panel) on duration of electrospinning in media including small fine fibers alone, media including commingled fibers of mixed diameters, or media including large fine fibers alone. The dotted lines indicate the best polynomial fit for the data; the corresponding equations are provided on the plots.

**[0048]** FIG. **4** shows an increase in basis weight observed with an increasing fraction of large fine fibers included within a media that includes commingled fibers of mixed diameters. Inset: linear increase in basis weight up to 10% large fine fiber content.

**[0049]** FIG. **5**A shows SEM images at 1,000× magnification for a series of fiber media samples of varying compositions (media including small diameter fibers only, media including layered fibers of mixed diameters with 2-20% large fine fibers, or media including large fine fibers only), as described in Example 5. The letters in each panel indicate the electrospinning sequence described in Table 1A. FIG. **5**B shows SEM images at 1,000× magnification for a series of fiber media samples of varying compositions (media including small diameter fibers only, media including commingled fibers of mixed diameters with 2-20% large fine fibers, or media including large fine fibers only), as described in Example 5. The letters in the panels of FIG. **5**A and FIG. **5**B indicate the electrospinning sequence described in Table 1A. FIG. **5**C shows a comparison of pore sizes (in micrometers (μm)), as measured by capillary flow porometry, for mixed diameter fiber media of varying composition and structure (top, fibers of mixed diameters within a single layer versus bottom panel, fibers of mixed diameters in separate layers). FIG. **5**D shows the effect of mean flow pore sizes (upper panel) and incorporation of large fine fibers into a mixed fiber diameter media (lower panel) on Figure of Merit (FOM). FIG. **5**E shows β values versus time elapsed (in minutes) for samples prepared and tested as described in Example 5 (a commingled layer of mixed fiber diameters (including 5% large fine fibers)). FIG. **5**F shows β values versus time elapsed (in minutes) for samples prepared and tested as described in Example 5 (a commingled layer of mixed fiber diameters (including 5% large fine fibers) deposited on a support layer of large fine fibers). FIG. **5**G shows a comparison of media pressure drop increase during test progression through media including commingled fibers of mixed diameters, as described in Example 5. The lower panel shows an enlarged view of a portion of the upper panel. FIG. **5**H shows a comparison of over-all β values for various dust particle sizes through media including commingled fibers of mixed diameters, as described in Example 5. The lower panel shows an enlarged view of a portion of the upper panel. FIG. **5**I shows a comparison of media pressure drop increase during test progression through media including layers of fibers of mixed diameters, as described in Example 5. The lower panel shows an enlarged view of a portion of the upper panel. FIG. **5**J shows a comparison of over-all β values for various dust particle sizes through media including layers of fibers of mixed diameters, as described in Example 5. The lower panel shows an enlarged view of a portion of the upper panel. FIG. **5**K shows pressure drop of clean media as the media composition is varied to include mixed fiber diameters wherein the fibers are commingled or layered.

**[0050]** FIG. **6**A shows an exemplary image of a media sample including 0.22 $g/m^2$ small fine fibers supported by 0.43 $g/m^2$ large fine fibers (for a total of 0.65 $g/m^2$), prepared as described in Example 6. The top layer of small fine fibers cover the underlying network of large fine fibers FIG. **6**B shows pressure drop during liquid filtration test time for media samples including varied basis weights (0.09 $g/m^2$, 0.10 $g/m^2$, 0.22 $g/m^2$, 0.31 $g/m^2$, 0.45 $g/m^2$, or 0.56 $g/m^2$) of small fine fibers supported by a fixed amount of large fine fibers, as described in Example 6. FIG. **6**C shows efficiencies for particulate contaminants of varying diameters for media samples including varied basis weights of small fine fibers (0.09 $g/m^2$, 0.10 $g/m^2$, 0.22 $g/m^2$, 0.31 $g/m^2$, 0.45 $g/m^2$, or 0.56 $g/m^2$) supported by a fixed amount of large fine fibers, as described in Example 6.

**[0051]** FIG. **7**A shows an exemplary image of a layered media sample prepared as described in Example 7 (a base layer of large fine fibers, followed by a layer of small fine fibers, then a layer of commingled small fine fibers and large fine fibers, and topped by a layer of large fine fibers (Large/Small/Commingled/Large, or L/S/Commingled/L); the commingled layer was prepared as described in Set I of Table 1A). The top layer of large fine fibers covers the layer that includes mixed small fine fiber and large fine fibers. FIG. **7**B shows an exemplary image of a cross-section of a layered media sample (L/S/L), prepared as described in Method 6 and Example 6. FIG. **7**C shows pressure drop during liquid filtration test time for media samples including layers of fibers of mixed diameters supported by large fine fibers, formed and tested as described in Example 7. FIG. **7**D shows over-all β values for particulate contaminants of media samples including layers of fibers of mixed diameters supported by large fine fibers, as described in Example 7.

**[0052]** FIG. **8**A shows a representative SEM image a network of commingled small fine fibers and large fine fibers deposited on top of a large fine fibers layer, formed as described in Example 8. FIG. **8**B shows pressure drop during liquid filtration test time for media samples including

a layer of commingled fibers of mixed diameters supported by large nanofibers, formed and tested as described in Example 8. FIG. **7**C shows over-all β values for particulate contaminants of a media samples including a layer of commingled fibers of mixed diameters supported by large fine fibers, formed and tested as described in Example 8.

**[0053]** FIG. **9**A and FIG. **9**B show pictorial representations of a cross-section of exemplary fine fibers including a polymer and a polymer-reactive resinous aldehyde composition showing, respectively, a three-phase structure and a two-phase structure.

**[0054]** FIG. **10**A and FIG. **10**B show pictorial representations of exemplary fine fibers including a polymer and a polymer-reactive resinous aldehyde composition showing, respectively, a three-phase structure and a two-phase structure.

**[0055]** FIG. **11**A and FIG. **11**B show the ratio of the total fine fiber basis weight to the average maximum pore size of the composite (that is, including a first layer, second layer, etc., of fine fibers) plotted against the basis weight of the second layer of fine fibers, as further described in Example 10. FIG. **11**B shows a subset of the samples of FIG. **11**A, allowing for a closer examination of the samples that did not survive Liquid Filtration Performance Testing without fine fiber damage (indicated by "x"). A dashed line indicates the slope of a line expected to delineate composites that can withstand Liquid Filtration Performance Testing and are unlikely to suffer fiber damage during use of a filtration layer, from composites that are likely to suffer fiber damage during use of a filtration layer. Circular data points indicate samples that survived Liquid Filtration Performance Testing without damage. Circular data points located below the dashed line correspond to media samples where a first layer of large fine fiber was deposited as described in Methods 4, 5, 6, and 7.

**[0056]** FIG. **12**A-FIG. **12**B shows initial pressure drop plotted against composite average maximum pore size (FIG. **12**A) or composite average mean flow pore size (FIG. **12**B) for composites including one or more layers of fine fiber and a support layer, as further described in Example 11. Triangles represent samples that maintained fine fiber structural integrity throughout testing; squares represent samples that suffered from fine fiber blow-out during testing.

**[0057]** FIG. **13**A shows representative SEM images of a network of layered 0.25 μm and 1.4 μm fibers deposited on top of a large fine fibers layer, formed as described in Example 12A. (That is, the "large" fine fibers have a fiber diameter 5.6 times the average fiber diameter of the "small" fine fibers.) FIG. **13**B shows representative SEM images of a network of commingled 0.25 μm and 1.4 μm fibers deposited on top of a large fine fibers layer, formed as described in Example 12A. FIG. **13**C shows a plot comparing of pore sizes for mixed diameter fine fiber media including commingled (circles) and layered (squares) 0.25 μm and 1.4 μm fibers prepared via pulsed spinning, as further described in Example 12A. FIG. **13**D shows the pressure drop in mixed diameter fine fiber media including layered 0.25 μm and 1.4 μm fibers prepared via pulsed spinning, as further described in Example 12A. FIG. **13**E shows the pressure drop in mixed diameter fine fiber media including commingled 0.25 μm and 1.4 μm fibers prepared via pulsed spinning, as further described in Example 12A. FIG. **13**F shows the efficiencies (over-all β) in mixed diameter fine fiber media including layered 0.25 μm and 1.4 μm fibers prepared via pulsed spinning, as further described in Example 12A. FIG. **13**G shows the efficiencies (over-all β) in mixed diameter fine fiber media including commingled 0.25 μm and 1.4 μm fibers prepared via pulsed spinning, as further described in Example 12A. In FIG. **13**D-FIG. **13**G, the bottom panel shows a zoomed in view of the lower left portion of the plot in the upper panel.

**[0058]** FIG. **13**H shows a plot comparing of pore sizes for mixed diameter fine fiber media including commingled (circles) and layered (squares) 0.25 μm and 1.4 μm fibers prepared via co-spinning, as further described in Example 12B. FIG. **13**I shows the pressure drop in mixed diameter fine fiber media including commingled 0.25 μm and 1.4 μm fibers prepared via co-spinning, as further described in Example 12B. FIG. **13**J shows the efficiencies (over-all (3) in mixed diameter fine fiber media including layered 0.25 μm and 1.4 μm fibers prepared via co-spinning, as further described in Example 12B. In FIG. **13**I-FIG. **13**J, the bottom panel shows a zoomed in view of the lower left portion of the plot in the upper panel.

**[0059]** FIG. **13**K shows a plot comparing of pore sizes for mixed diameter fine fiber media including 0.25 μm and 1.4 μm fibers including in a L/S/Commingled/L structure, as further described in Example 12C. FIG. **13**L shows the pressure drop in mixed diameter fine fiber media including commingled 0.25 μm and 1.4 μm fibers prepared via co-spinning, as further described in Example 12C. FIG. **13**M shows the efficiencies (over-all β) in mixed diameter fine fiber media including layered 0.25 μm and 1.4 μm fibers prepared via co-spinning, as further described in Example 12C. In FIG. **13**L-FIG. **13**M, the bottom panel shows a zoomed in view of the lower left portion of the plot in the upper panel.

**[0060]** FIG. **14**A shows representative SEM images of a network of layered 0.5 μm and 1.4 μm fibers deposited on top of a large fine fibers layer, formed as described in Example 13A. (That is, the "large" fine fibers have a fiber diameter 2.8 times the average fiber diameter of the "small" fine fibers.) FIG. **14**B shows representative SEM images of a network of commingled 0.5 μm and 1.4 μm fibers deposited on top of a large fine fibers layer, formed as described in Example 13A. FIG. **14**C shows a plot comparing of pore sizes for mixed diameter fine fiber media including commingled (circles) and layered (squares) 0.5 μm and 1.4 μm fibers prepared via pulsed spinning, as further described in Example 13A. FIG. **14**D shows a plot comparing of Figure of Merit (FOM) for mixed diameter fine fiber media including commingled (circles) and layered (squares) 0.5 μm and 1.4 μm fibers prepared via pulsed spinning, as further described in Example 13A. FIG. **14**E shows the pressure drop in mixed diameter fine fiber media including layered 0.5 μm and 1.4 μm fibers prepared via pulsed spinning, as further described in Example 13A. FIG. **14**F shows the pressure drop in mixed diameter fine fiber media including commingled 0.5 μm and 1.4 μm fibers prepared via pulsed spinning, as further described in Example 13A. FIG. **14**G shows the efficiencies (over-all β) in mixed diameter fine fiber media including layered 0.5 μm and 1.4 μm fibers prepared via pulsed spinning, as further described in Example 13A. FIG. **14**H shows the efficiencies (over-all β) in mixed diameter fine fiber media including commingled 0.25 μm and 1.4 μm fibers prepared via pulsed spinning, as further described in Example 13A. In FIG. **14**E-FIG. **14**H,

the bottom panel shows a zoomed in view of the lower left portion of the plot in the upper panel.

**[0061]** FIG. **14**I shows a comparison of the efficiency (% Penetration, left axis) and Figure of Merit (FOM, right axis) for filter media including mixed 0.5 μm and 1.4 μm fibers prepared via co-spinning, as further described in Example 13B.

**[0062]** FIG. **15**A shows a cross-plot of % improvement in initial dP and β value for 3 um particles for all mixed diameter fiber media structures (squares), as described in Example 14, compared to a glass fiber-containing media with β=1000 for <4 um (circle at origin). FIG. **15**B shows a plot comparing initial dP in various mixed fiber media and glass fiber-containing media (circles), across contaminant sizes at which the β rating is 1000, as further described in Example 14.

**[0063]** FIG. **16**A shows an exemplary cross-sectional image of a fine fiber layer on a support layer. FIG. **16**B-FIG. **16**D show exemplary images of a method to measure the fine fiber layer thickness, as further described in the Examples.

## DETAILED DESCRIPTION OF ILLUSTRATIVE EMBODIMENTS

**[0064]** This disclosure describes a high performing (including, for example, high efficiency and low pressure drop) filter media. In some embodiments, this disclosure describes filter media that achieves the efficiency of filter media that includes fine glass fibers without the inclusion of fine glass fibers. The filter media includes a support layer and a fine fiber layer. The fine fiber layer includes at least one layer of fine fibers but may, optionally, include multiple layers of fine fibers. The fine fibers included in the filter media have mixed diameters such that the fine fiber layer includes "large" fine fibers having a fiber diameter at least 3 times the average fiber diameter of a "small" fine fiber. The "large" fine fibers have an average diameter of at least 1 μm or greater than 1 μm. In some embodiments, the filter media is substantially free of glass or does not include glass.

**[0065]** High efficiency filter media typically include fine glass fibers. The glass fibers provide pore size control and cooperate with the other fibers in the media to provide a media of substantial flow rate, high capacity, substantial efficiency and high wet strength. However, when used in fuel or hydraulic filters, glass fibers may be shed from the media, resulting in abrasion in the engine.

**[0066]** Replacing fine glass fibers with other fine fibers has proved a challenge, however. In particular, including enough non-glass fine fibers to achieve the same efficiency as a media with fine glass fibers typically results in such a thick or high density fine fiber layer that the media has a low permeability, resulting in pressure drops that rise to levels associated with shorter filter life and greater energy use.

**[0067]** Moreover, when using thinner or lower density layers of fine fibers, although the desired efficiency may be transiently achieved and permeability may be improved to achieve acceptable pressure drop values, the efficiency of such a fine fiber layer typically collapses as pressure drop is increased during the lifetime of the filter. This drop in efficiency is thought to be due to a "blow out" of the fiber layer and is reflected by a loss in β. (See FIG. **1**A & FIG. **1**F.) Additionally, when analyzed using scanning electron microscopy (SEM) after an efficiency collapse, damage to the nanofiber fiber layer can be observed. (See FIG. **1**B.)

**[0068]** Without wishing to be bound by theory, it is believed that efficiency collapse seen when using thinner or lower density layers of fine fibers is a result of variances in the underlying support layer that result in a variety of pore sizes that must be spanned by the fine fibers. In locations where the pore size of the underlying support layer is large, and the span of the fine fiber too great, breakage of the fine fiber occurs during use, resulting in loss of efficiency.

**[0069]** Although more uniform support layers exist, the expense of such layers makes their use in filtration media cost prohibitive. Moreover, more uniform layers do not always exhibit the robustness required for manufacturing of a filter media including web-handling capability. In contrast, spunbond support layers, for example, while exhibiting large variances in pore sizes are otherwise cheap and robust layers, making them especially suitable for use as a support layer in a filter media.

**[0070]** As noted above, the fine fibers included in the filter media of this disclosure have mixed diameters such that the fine fiber layer includes "large" fine fibers having an average fiber diameter at least 3 times the average fiber diameter of a "small" fine fiber. In some embodiments, the "large" fine fibers have a fiber diameter of up to 6 times the average fiber diameter of a "small" fine fiber. Without wishing to be bound by theory, it is believed that the larger diameter fine fibers provide support for the smaller diameter fine fibers, allowing the smaller diameter fine fibers to span pores in the underlying support layer and resist fiber "blow out" even when the media is exposed to higher pressures. Moreover, the smaller diameter fine fibers allow for the formation of smaller pores, permitting higher efficiency values to be achieved. See, for example, Wang et al., Physical Review Materials, 2020, 4:083803.

**[0071]** Unexpectedly, including large fine fibers that have an average fiber diameter at least 3 times the average fiber diameter of a small fine fiber provided the best combination of efficiency and pressure drop. Although a fine fiber layer including large fine fibers that have an average fiber diameter of approximately 2.8 times the average fiber diameter of a small fine fiber provided better fiber survivability than a fine fiber layer using small fine fibers alone, the filter media did not exhibit the same level of performance observed with the mixed diameter fine fibers where the large fine fibers that have an average fiber diameter at least 3 times the average fiber diameter of a small fine fiber. (See Examples 13 and 14.)

**[0072]** In some embodiments, the large fine fibers may have a diameter at least 0.2 μm, at least 0.3 μm, or at least 0.4 μm greater than a diameter of the small fine fibers. Although, as noted above, the large fine fibers have an average fiber diameter at least 3 times the average fiber diameter of a small fine fiber, either or both of the large fine fibers and the small fine fibers may include a distribution of fibers of varying sizes that provide the average diameter. When the large fine fibers and the small fine fibers include, for example, a distribution of sizes, the diameter of the smallest-diameter large fine fibers may be at least 0.2 μm, at least 0.3 μm, or at least 0.4 μm greater than the diameter of the largest-diameter small fine fibers. In some such embodiments, the large fine fibers and the small fine fibers may form a bimodal distribution. In some embodiments, the large fine fibers may have a diameter of up to 1 μm, up to 2 μm, or up to 3 μm greater than the diameter of small fine fibers. In an exemplary embodiment, the diameter of the smallest-diam-

eter large fine fibers may be up in a range of 0.2 μm to 2 μm greater than the diameter of the largest-diameter small fine fibers.

**[0073]** In some embodiments, as further described herein, the fine fiber layer includes a single (or first) fine fiber layer that includes a both large fine fibers having a fiber diameter at least 3 times the average fiber diameter of a small fine fiber (see FIG. **1**G). In some embodiments, the fine fiber layer may include multiple layers (for example, a first fine fiber layer, a second fine fiber layer, etc.).

**[0074]** In some embodiments, the total thickness of the fine fiber layer is up to 5 μm, up to 10 μm, up to 30 μm, or up to 50 μm. Without wishing to be bound by theory, it is believed that exceeding 50 μm in fine fiber layer thickness will result in a media having an undesirably high pressure drop. In some embodiments, when minimizing pressure drop is desired, thinner fine fiber layer thicknesses (for example, up to 5 μm thick, up to 10 μm thick, or up to 30 μm thick) may be preferred.

**[0075]** In some embodiments, the total thickness of the fine fiber layer may be measured using scanning electron microscopy (SEM). For example, a sample including at least the fine fiber layer and the support layer may be prepared for SEM by cross-sectioning the sample while frozen (for example, in liquid nitrogen). It may be useful to cross-section the sample while the sample is oriented with the support layer being cut before the fine fiber layer. It may further be useful to cross-section the sample while the sample is submerged in liquid nitrogen. An exemplary magnification that may be used is 1000×. It may be useful to use software to assist with the determination of sample thickness by allowing for outlining and re-shading of the fine fiber section in the SEM image. The re-shaded image may then be used to determine the maximal thickness of the fine fiber section in the image. In some embodiments, the total thickness of the fine fiber layer may be determining by averaging at least five maximal thicknesses from five separate images of the same sample.

**[0076]** In one exemplary embodiment, a first layer of fine fibers may include predominantly large fine fibers and a second layer of fine fibers may include predominantly small fine fibers. For example, the first layer of fine fibers may include up to 10% or up to 20% large fine fibers (that is, fine fibers having a fiber diameter at least 3 times the average fiber diameter of the smaller diameter fibers). In some embodiments, including when the first layer of fine fibers is made up of large fine fibers or includes predominantly large fine fibers, the second layer of fine fibers may include up to 10% or up to 20% larger diameter fine fibers (that is, fine fibers having a fiber diameter at least 3 times the average fiber diameter of the smaller fibers).

**[0077]** Without wishing to be bound by theory, it is believed that replacing a small proportion of the small diameter fine fibers of a fine fiber layer made up predominantly of smaller diameter nanofibers with larger diameter nanofibers may open up the nonwoven structure and increase the permeability and the potential for depth loading of the second layer of fine fibers while retaining efficiencies attributed to the network of smaller diameter nanofibers.

**[0078]** In some embodiments, as further discussed herein, the large fine fiber and the small fine fiber may be commingled within a single fine fiber layer. Such commingling decreases the solidity of the fine fiber layer compared with a fine fiber layer that only includes small fine fibers. Without wishing to be bound by theory, it is believed this decreased solidity is seen because the large fine fibers act as spacers, allowing for more air movement between the fibers.

**[0079]** The filter media described herein provide low initial dP values and do not exhibit an efficiency or β collapse through the expected lifetime of the filter. (See Example 1 and FIG. **1**C.) Additionally, when analyzed using SEM, damage to the fine fiber layer when the media layer is exposed to pressure (including, for example, up to 20 psi) is minimized. (See FIG. **1**D.)

Support Layer

**[0080]** The filter media described herein include a support layer (also referred to herein as a substrate). The support layer may include or be made of any suitable porous material.

**[0081]** Typically, fibrous materials will be used for the support layer. The fibers of the support layer may be made of natural fiber and/or synthetic fibers. Suitable fibers may include cellulosic fiber, glass fibers, metal fibers, or synthetic polymeric fibers, or a combination or mixture thereof.

**[0082]** In certain embodiments, the support layer includes fibers having an average diameter of at least 5 microns, or at least 10 microns. In some embodiments, the support layer can include fibers having an average diameter of up to 250 microns.

**[0083]** In some embodiments, the support layer is at least 0.005 inch (125 microns) thick, and often at least 0.01 inch (250 microns) thick. In some embodiments, the support layer is up to 0.03 inch (750 microns) thick.

**[0084]** In some embodiments, the support layer has a basis weight of at least 8 $g/m^2$, at least 10 $g/m^2$, at least 15 $g/m^2$, or at least 20 $g/m^2$. In some embodiments, the support layer has a basis weight of up to 70 $g/m^2$, up to 100 $g/m^2$, or up to 150 $g/m^2$. In an exemplary embodiment, the support layer has a basis weight in a range of 8 $g/m^2$ to 150 $g/m^2$. In another exemplary embodiment, the support layer has a basis weight in a range of 15 $g/m^2$ to 100 $g/m^2$. The basis weight of the support layer may be measured using TAPPI T410 om-08.

**[0085]** In some embodiments, the support layer has a solidity of at least 5%, at least 10%, at least 20%, at least 25%, at least 30%, or at least 40%. In some embodiments, the support layer has a solidity of up to 10%, up to 20%, up to 25%, up to 30%, up to 40%, or up to 50%. In an exemplary embodiment, the support layer has a solidity in a range of 10% to 40%. In another exemplary embodiment, the support layer has a solidity in a range of 20% to 30%. The solidity of the support layer may be calculated using the equation $c=BW/\rho Z$, where BW is the basis weight, measured using TAPPI T410 om-08; p is the density of the fiber; and Z is the thickness of the media, measured according to TAPPI T411 om-15. When measuring thickness of the media, a foot pressure of 1.5 psi may be used.

**[0086]** In some embodiments, the support layer has an average mean flow pore size of at least 5 μm, at least 10 μm, at least 15 μm, at least 20 μm, or at least 25 μm. In some embodiments, the support layer has an average mean flow pore size of up to 10 μm, up to 15 μm, up to 20 μm, up to 25 μm, up to 30 μm, up to 35 μm, up to 40 μm, up to 50 μm, up to 60 μm, up to 70 μm, up to 80 μm, or up to 90 μm. In an exemplary embodiment, the support layer has an average mean flow pore size in a range of 10 μm to 25 μm. In some

embodiments, the average mean flow pore size is preferably determined using capillary flow porometry.

**[0087]** In some embodiments, the support layer has an average maximum pore size of up to 10 μm, up to 15 μm, up to 20 μm, up to 25 μm, up to 30 μm, up to 35 μm, up to 40 μm, up to 50 μm, up to 60 μm, up to 70 μm, up to 80 μm, up to 90 μm, up to 100 μm, or up to 150 μm. In an exemplary embodiment, the support layer has an average maximum pore size of up to 90 μm. In some embodiments, the average maximum pore size is preferably determined using capillary flow porometry.

**[0088]** In some embodiments, the support layer has an average minimum pore size of at least 5 μm, at least 10 μm, at least 15 μm, at least 20 μm, at least 25 μm, at least 30 μm, at least 35 μm, at least 40 μm, or at least 50 μm. In an exemplary embodiment, the support layer has an average minimum pore size of at least 20 μm. In some embodiments, the average minimum pore size is preferably determined using capillary flow porometry.

**[0089]** In some embodiments, the support layer preferably includes a consistent media structure—that is, the features of the media (including, for example, the pore size, solidity, basis weight, or thickness, or a combination of those features, or each of these features of the media) are consistent across the length and width of the media. For example, in an exemplary embodiment, the average mean flow pore size does not vary by more than 30%, more preferably 25%, and even more preferably 15% across the length and width of the media.

**[0090]** In some embodiments, however, Moreover, as noted, above, at least one aspect of consistency or uniformity (for example, pore size consistency) may be sacrificed for the robustness required for manufacturing of a filter media (including web-handling capability). For example, spunbond support layers, while exhibiting large variances in pore sizes are otherwise cheap and robust layers, making them especially suitable for use as a support layer in a filter media.

**[0091]** Without wishing to be bound by theory, it is believed that the interplay between the fiber diameter of fine fiber layer (particularly, the first layer of fine fibers), the thickness of fine fiber layer, and the maximum pore size of the support layer is critical to achieving a structurally sound and efficient media. For example, merely using a higher basis weight (for example, greater than 60 g/m$^2$) support layer does not result in a structurally sound media because, if the maximum pore sizes of the support layer are above a certain size (for example, 90 μm), if the fine fiber diameters are below a certain size, and/or if the fine fiber thickness is small, the fine fiber layer will be structurally compromised during filtration at a sufficiently high pressure drop. For example, when smaller fine fibers (for example, having an average diameter of up to 0.5 μm) were used for the first fine fiber layer on a support layer having an average maximum pore size of 88 μm, increasing the basis weight of the fine fiber layer was found to require an unsustainably high pressure to move fluid through the media; in contrast, decreasing the basis weight of the smaller fine fiber layer caused the layer to become structurally compromised during filtration. Although increasing the fiber size of at least one of the fibers in the first fine fiber layer (for example, to an average diameter of at least 0.6 μm, more preferably, at least 0.9 μm, even more preferably, at least 1 μm) deposited on a support layer having an average maximum pore size of 88 μm decreased the efficiency of the media, increasing the fiber size also decreased pressure drop and resulted in a structurally sound media that does not become structurally compromised during use.

**[0092]** As further described in Example 10, plotting the ratio of the total fine fiber basis weight to the average maximum pore size of the overall composite was plotted against the basis weight of the second layer of fine fibers may allow for the identification of the features (fine fiber basis weight and average maximum pore size of the overall composite) that correlate with a fine fiber layer likely to experience damage during FHAST bench testing. As shown in FIG. **11**, composites that can withstand Liquid Filtration Performance Testing and are unlikely to suffer fiber damage during use of a filtration layer can be delineated from composites that are likely to suffer fiber damage during use of a filtration layer.

**[0093]** The support layer may be formed of any suitable material. Examples of suitable material for the support layer include spunbond, wetlaid, carded, or melt-blown nonwoven materials, or combinations thereof including, for example, a spunbond-meltblown-spunbond. Fibers can be in the form of wovens or nonwovens. Examples of synthetic nonwovens include polyester nonwovens, nylon nonwovens, polyolefin (for example, polypropylene) nonwovens, polycarbonate nonwovens, or blended or multicomponent nonwovens thereof. Sheet-like support layers (for example, cellulosic, synthetic, and/or glass or combination webs) are typical examples of filter support layers. Other examples of suitable support layers include polyester or bicomponent polyester fibers or polypropylene/polyethylene terephthalate, or polyethylene/polyethylene terephthalate bicomponent fibers in a spunbond.

**[0094]** In some embodiments, the support layer may preferably include polymer fibers. In some embodiments, the polymer fibers may include nylon fiber or polyester fibers.

**[0095]** In some embodiments, the support layer may preferably include spunbond fibers.

**[0096]** In one exemplary embodiment, the support layer may be a nylon scrim.

**[0097]** In an exemplary embodiment, the support layer includes CEREX 23200 (Cerex Advanced Fabrics, Inc., Cantoment, Fla.). CEREX 23200 includes nylon 6,6, has a thickness of 8.4 mils (0.21 mm), a basis weight of 67.8 g/m$^2$, a solidity of 28%, and a permeability per solidity of 615.1. Pore sizes for CEREX 23200 are shown in Table 2C.

Fine Fiber Layer

**[0098]** The filter media described herein includes a fine fiber layer. The fine fiber layer always includes a first layer of fine fibers (also referred to as a first fine fiber layer) that is deposited on the support layer. As further discussed herein, the fine fiber layer may, optionally, also include one or more additional layers of fine fibers. For example, the fine fiber layer may include a second layer of fine fibers (also referred to as a second fine fiber layer), wherein the second layer of fine fibers is deposited on the first layer of fine fibers.

**[0099]** In some embodiments, the fine fiber layer may have a thickness of at least 2 μm, at least 3 μm, at least 4 μm, or at least 5 μm.

**[0100]** In some embodiments, the fine fiber layer may have a thickness of up to 5 μm, up to 10 μm, up to 30 μm, or up to 50 μm.

**[0101]** In some embodiments, the total thickness of the fine fiber layer may be measured using scanning electron microscopy (SEM). For example, a sample including at least the fine fiber layer and the support layer may be prepared for SEM by cross-sectioning the sample while frozen (for example, in liquid nitrogen). It may be useful to cross-section the sample while the sample is oriented with the support layer being cut before the fine fiber layer. It may further be useful to cross-section the sample while the sample is submerged in liquid nitrogen. An exemplary magnification that may be used is 1000×. It may be useful to use software to assist with the determination of sample thickness by allowing for outlining and re-shading of the fine fiber section in the SEM image. The re-shaded image may then be used to determine the maximal thickness of the fine fiber section in the image. In some embodiments, the total thickness of the fine fiber layer may be determining by averaging at least five maximal thicknesses from five separate images of the same sample.

First Layer of Fine Fibers

**[0102]** In some embodiments, the first layer of fine fibers includes "large" fine fibers having an average diameter at least 3 times the average fiber diameter of a "small" fine fiber. That is, the first layer of fine fibers may include fibers of mixed diameters.

**[0103]** Additionally or alternatively, a small fine fiber may be present in a second layer of fine fibers. When the small fine fiber is present in the second layer of fine fibers but not the first layer of fine fibers, the first layer of fine fibers may include only "large" fine fibers having an average diameter at least 3 times the average fiber diameter of the smallest average fiber diameter of the second fine fiber layer. In such embodiments, the large fine fibers of the first fine fiber layer may have a diameter at least 0.2 μm, at least 0.3 μm, or at least 0.4 μm greater than a diameter of a fiber of the second fine fiber layer. Although, as noted above, the large fine fibers have an average fiber diameter at least 3 times the average fiber diameter of a small fine fiber, either or both of the large fine fibers and the small fine fibers may include a distribution of fibers of varying sizes that provide the average diameter. When the large fine fibers of the first fine fiber layer and the small fine fibers of the second fine fiber layer include, for example, a distribution of sizes, the diameter of the smallest-diameter large fine fibers may be at least 0.2 μm, at least 0.3 μm, or at least 0.4 μm greater than the diameter of the largest-diameter small fine fibers. In some embodiments, the large fine fibers of the first fine fiber layer may have a diameter of up to 1 μm, up to 2 μm, or up to 3 μm greater than the diameter of small fine fibers.

**[0104]** In some embodiments, the "large" fine fibers of the first layer of fine fibers preferably have an average diameter of at least 1 μm or greater than 1 μm. The "large" fine fibers of the first layer of fine fibers have an average diameter of up to 1.1 μm, up to 1.2 μm, up to 1.3 μm, up to 1.4 μm, up to 1.5 μm, up to 2 μm, up to 3 μm, up to 4 μm, up to 5 μm, or up to 10 μm. Exemplary images of a first fine fiber layer include large fine fibers deposited on a support layer are shown in FIG. **1**E.

**[0105]** In embodiments where the first fine fiber layer includes "large" fine fibers and "small" fine fibers, and wherein the large fine fibers have an average diameter at least 3 times the average fiber diameter of the small fine fibers, the small fine fibers may have an average diameter of up to 0.3 μm, up to 0.4 μm, up to 0.5 μm, or up to 0.6 μm. In some embodiments, the average fiber diameter of the small fine fibers of the first fine fiber layer may be at least 0.2 μm. For example, the average fiber diameter of the small fine fibers may be in a range of 0.2 μm to 0.6 μm, in a range of 0.3 μm to 0.5 μm, or in a range of 0.2 μm to 0.3 μm.

**[0106]** In such embodiments, the large fine fibers of the first fine fiber layer may have a diameter at least 0.2 μm, at least 0.3 μm, or at least 0.4 μm greater than a diameter of the small fine fibers of the first fine fiber layer. Although, as noted above, the large fine fibers have an average fiber diameter at least 3 times the average fiber diameter of a small fine fiber, either or both of the large fine fibers and the small fine fibers may include a distribution of fibers of varying sizes that provide the average diameter. When the large fine fibers of the first fine fiber layer and the small fine fibers of the first fine fiber layer include, for example, a distribution of sizes, the diameter of the smallest-diameter large fine fibers may be at least 0.2 μm, at least 0.3 μm, or at least 0.4 μm greater than the diameter of the largest-diameter small fine fibers. In some such embodiments, the large fine fibers and the small fine fibers may form a bimodal distribution. In some embodiments, the large fine fibers of the first fine fiber layer may have a diameter of up to 1 μm, up to 2 μm, or up to 3 μm greater than the diameter of small fine fibers of the first fine fiber layer.

**[0107]** Exemplary combinations of "large" fine fiber and "small" fine fiber diameters include, for example, 1 μm and 0.25 μm diameter fibers (see Examples 1-11); or 1.4 μm and 0.25 μm diameter fibers (see Example 12). Although Example 13 further discloses 1.4 μm and 0.5 μm diameter fibers, it is noted that the large fine fibers (1.4 μm) do not have an average diameter at least 3 times the average fiber diameter of the small fine fibers (0.5 μm).

**[0108]** Without wishing to be bound by theory, it is believed that the inclusion of a layer of fine fibers including large fine fibers allows for the use of a more "open" support layer than filter media without a layer including large fine fibers. The use of a more "open" support layer provides lower pressure drops than a support layer with smaller pores or higher basis weight because the material passing through the filter encounters less material to hinder the flow.

First Layer of Fine Fibers—Large Fine Fiber

**[0109]** In some embodiments, the first layer of fine fibers includes predominately (for example, more than 95%) large fine fibers or does not include small fine fibers. In such embodiments, a second layer of fine fibers including small fine fibers, as described below, is deposited on the first layer of fibers.

**[0110]** In such embodiments, the large fine fibers of the first fine fiber layer may have a diameter at least 0.2 μm, at least 0.3 μm, or at least 0.4 μm greater than the diameter of the small fine fibers of the second fine fiber layer. Although, as noted above, the large fine fibers have an average fiber diameter at least 3 times the average fiber diameter of a small fine fiber, either or both of the large fine fibers and the small fine fibers may include a distribution of fibers of varying sizes that provide the average diameter. When the large fine fibers of the first fine fiber layer and the small fine fibers of the second fine fiber layer include, for example, a distribution of sizes, the diameter of the smallest-diameter large fine fibers may be at least 0.2 μm, at least 0.3 μm, or at least 0.4 μm greater than the diameter of the largest-

diameter small fine fibers. In some such embodiments, the large fine fibers and the small fine fibers may form a bimodal distribution. In some embodiments, the large fine fibers of the first fine fiber layer may have an average diameter of up to 1 μm, up to 2 μm, or up to 3 μm the average diameter of small fine fibers of the second fine fiber layer.

**[0111]** In some embodiments, including when the filter media includes a second layer of fine fibers, the first layer of fine fibers has a basis weight of at least 0.005 $g/m^2$, at least 0.01 $g/m^2$, at least 0.05 $g/m^2$, at least 0.1 $g/m^2$, at least 0.5 $g/m^2$, at least 1 $g/m^2$, at least 1.5 $g/m^2$, at least 2 $g/m^2$, or at least 2.5 $g/m^2$. In some embodiments, the first layer of fine fibers has a basis weight of up to 1.5 $g/m^2$, up to 2 $g/m^2$, up to 2.5 $g/m^2$, up to 3 $g/m^2$, up to 3.5 $g/m^2$, up to 4 $g/m^2$, up to 4.5 $g/m^2$, up to 5 $g/m^2$, up to 10 $g/m^2$, up to 15 $g/m^2$, up to 20 $g/m^2$, up to 25 $g/m^2$, up to 50 $g/m^2$. In some embodiments, the first layer of fine fibers has a basis weight of at least 0.1 $g/m^2$ and up to 20 $g/m^2$. In another exemplary embodiment, the first layer of fine fibers has a basis weight of at least 0.1 $g/m^2$ and up to 1 $g/m^2$. In a further exemplary embodiment, the first layer of fine fibers has a basis weight 0.25 $g/m^2$. Basis weight of the fine fibers may be calculated from the mass of the fine fibers and the area of the scrim, according to the following equation: Total basis weight of the fine fiber layers=(mass of the fine fibers)/(area of scrim). The mass of the fine fibers may be calculated from the polymer and spinning conditions used to make the fiber, according to the following equation: mass of fine fibers=(% w/v polymer in solution)×(pump rate)×(spinning time).

**[0112]** In some embodiments, including when the filter media includes a second layer of fine fibers, the first layer of fine fibers has an average mean flow pore size of at least 5 μm, at least 10 μm, at least 15 μm, or at least 20 μm. In some embodiments, the first layer of fine fibers has an average mean flow pore size of up to 10 μm, up to 15 μm, up to 20 μm, up to 25 μm, up to 30 μm, or up to 35 μm. In an exemplary embodiment, the first layer of fine fibers has an average mean flow pore size in a range of 10 μm to 25 μm. In some embodiments, the average mean flow pore size is preferably determined using capillary flow porometry.

**[0113]** In some embodiments, including when the filter media includes a second layer of fine fibers, the first layer of fine fibers has an average maximum pore size of up to 10 μm, up to 15 μm, up to 20 μm, up to 25 μm, up to 30 μm, or up to 35 μm. In some embodiments, the average maximum pore size of the first layer of fine fibers is preferably determined using capillary flow porometry.

**[0114]** In some embodiments, including when the filter media includes a second layer of fine fibers, the first layer of fine fibers has a thickness of at least the average diameter of a large fine fiber of the first layer of fine fibers. In some embodiments, the first layer of fine fibers has a thickness of at least 0.7 μm, at least 1 μm, at least 2 μm, or at least 5 μm.

**[0115]** In some embodiments, the first layer of fine fibers has a thickness that is the thickness of a several fibers having the average diameter of the large fine fiber of the first layer of fine fibers. For example, the first layer of fine fibers may have a thickness of at least 2 μm, at least 3 μm, at least 4 μm, or at least 5 μm. In some embodiments, the first layer of fine fibers has a thickness of greater than 1 μm.

**[0116]** In some embodiments, the first layer of fine fibers has a thickness of up to 5 μm, up to 10 μm, up to 30 μm, or up to 50 μm.

**[0117]** In some embodiments, the total thickness of the fine fiber layer may be measured using scanning electron microscopy (SEM). For example, a sample including at least the fine fiber layer and the support layer may be prepared for SEM by cross-sectioning the sample while frozen (for example, in liquid nitrogen). It may be useful to cross-section the sample while the sample is oriented with the support layer being cut before the fine fiber layer. It may further be useful to cross-section the sample while the sample is submerged in liquid nitrogen. An exemplary magnification that may be used is 1000×. It may be useful to use software to assist with the determination of sample thickness by allowing for outlining and re-shading of the fine fiber section in the SEM image. The re-shaded image may then be used to determine the maximal thickness of the fine fiber section in the image. In some embodiments, the total thickness of the fine fiber layer may be determining by averaging at least five maximal thicknesses from five separate images of the same sample.

**[0118]** In some embodiments, including when the filter media include a second layer of fine fibers, the first layer of fine fibers may have a solidity lower than the solidity of the second layer of fine fibers. That is, the first layer of fine fibers may preferably be more open than the second layer of fine fibers. In some embodiments, the first layer of fine fibers has a solidity of at least 0.1%, at least 0.5%, at least 1%, at least 5%, at least 10%, at least 20%, at least 25%, at least 30%, or at least 40%. In some embodiments, the first layer of fine fibers has a solidity of up to 10%, up to 20%, up to 25%, up to 30%, up to 40%, or up to 50%. In an exemplary embodiment, the first layer of fine fibers has a solidity in a range of 0.1% to 40%. In another exemplary embodiment, the first layer of fine fibers has a solidity in a range of 0.1% to 20%. Solidity (c) of the fine fiber layer may be calculated from the dimensionless fiber drag parameter, F*1.0, using the following equation: $F^*_{1.0}=4.3548e^{8.8822c}$. $F^*_{1.0}$ may be calculated from a modified Kirsch-Fuchs equation, as further described in the Examples.

First Layer of Fine Fibers—Mixed Diameter Fine Fibers

**[0119]** In some embodiments, the first layer of fine fibers includes large fine fibers and small fine fibers, wherein the large fine fibers have an average diameter at least 3 times the average fiber diameter of the small fine fibers. In such embodiments, a second layer of fine fibers, as described below, may or may not be deposited on the first layer of fibers.

**[0120]** In some embodiments, the large fine fibers of the first fine fiber layer may have a diameter at least 0.2 μm, at least 0.3 μm, or at least 0.4 μm greater than a diameter of a small fine fiber of the first fine fiber layer. Although, as noted above, the large fine fibers have an average fiber diameter at least 3 times the average fiber diameter of a small fine fiber, either or both of the large fine fibers and the small fine fibers may include a distribution of fibers of varying sizes that provide the average diameter. When the large fine fibers or the small fine fibers include a distribution of sizes, the diameter of the smallest-diameter large fine fibers may be at least 0.2 μm, at least 0.3 μm, or at least 0.4 μm greater than the diameter of the largest-diameter small fine fibers. In some embodiments, the large fine fibers may have a diameter of up to 1 μm, up to 2 μm, or up to 3 μm greater than the diameter of the small fine fibers.

**[0121]** When the first layer of fine fibers includes both small fine fibers and large fine fibers, the layer may include any suitable mixture of fibers of mixed diameters. Exemplary layered fiber structures that may be used for the first layer of fine fibers include one or more of Set A5, Set B, Set D5, Set E, Set I5, or Set J, of Table 1A-Table 1C. Exemplary commingled fiber structures that may be used for the second layer of fine fibers include one or more of Set A6, Set D, Set D6, Set I, or Set L, of Table 1A-Table 1C.

**[0122]** When the first layer of fine fibers includes both small fine fibers and large fine fibers, the fibers of mixed diameters may be commingled (as a result of having been formed simultaneously) (see FIG. **1**I), or layered (as a result of having been alternately applied to a substrate) (see FIG. **1**J and FIG. **1**L), or both (see FIG. **1**M). When the fibers of mixed diameters are layered (as a result of having been alternately applied to a substrate), then a single layer of fine fibers may include sub-layers of large fine fibers and small fine fibers.

**[0123]** In some embodiments, the first layer of fine fibers may include at least 0.5% large fine fibers, at least 1% large fine fibers, at least 2% large fine fibers, at least 5% large fine fibers, at least 7% large fine fibers, at least 10% large fine fibers, at least 12% large fine fibers, at least 14% large fine fibers, at least 16% large fine fibers, at least 20% large fine fibers, at least 50% large fine fibers, at least 60% large fine fibers, at least 70% large fine fibers, or at least 80% large fine fibers. In some embodiments, the first layer of fine fibers may include up to 1% large fine fibers, up to 2% large fine fibers, up to 5% large fine fibers, up to 7% large fine fibers, up to 10% large fine fibers, up to 12% large fine fibers, up to 14% large fine fibers, up to 16% large fine fibers, up to 20% large fine fibers, up to 50% large fine fibers, up to 60% large fine fibers, up to 70% large fine fibers, up to 80% large fine fibers, or up to 90% large fine fibers. Some exemplary mixtures are shown in Table 1A-Table 1C. For example, the first layer of fine fibers may include the proportion of large fine fibers of one or more of Set A5, Set A6, Set B, Set D, Set D5, Set D6, Set E, Set I, Set I5, Set I6, Set J, or Set L of Table 1A-Table 1C. Additional exemplary ranges of large fine fibers in the first layer of fine fibers include 10% to 90% large fine fibers, 20% to 80% large fine fibers, or 30% to 70% large fine fibers.

**[0124]** In some embodiments, the proportion of large fine fibers may be estimated from the diameters of small and large fine fibers, % solids in precursor spinning solutions, syringe pump feed rates, and electrospinning time.

**[0125]** In some embodiments, the proportion of large fine fibers may be determined based on spin time using the equation provided in the Fiber Proportion Calculation section of the Examples.

**[0126]** In some embodiments, the proportion of large fine fibers may be determined by nano-computed tomography (nano-CT). For example, a sample of the filter media may be embedded in resin scanned as if slicing along the Z-axis. Useful images may be obtained by using, for example, a synchrotron-quality Nanoscale 3D X-ray Imaging machine such as Xradia 810 Ultra (Zeiss, Oberkochen, Germany). It may be useful to then stitch the images together, forming a 3D digital structure in order to use the digital structure to determine proportion of fibers having a particular diameter. The proportion of small/large fine fibers may be calculated by taking the ratio of the small/large fine fiber count against the total fiber (both small and large) count within the digital structure.

**[0127]** In some embodiments, the proportion of large fine fibers may be determined using microscopy. For example, sample images may be obtained via SEM at appropriate magnification (for example, 500×, 1000×, or 2500×). The presence of one or more fiber populations may be determined by counting all fibers within the image, followed by classifying into small fine fibers and large fine fibers based on grouping diameters within 25% variation. Fiber size may be measured and/or classified using image processing software such as ImageJ. The proportion of small/large fine fibers may be calculated by taking the ratio of the small/large fine fiber count against the total fiber (both small and large) count within the image.

**[0128]** In some embodiments, the first layer of fine fibers has an average mean flow pore size of at least 0.1 μm, at least 0.5 μm, at least 1 μm, at least 5 μm, at least 10 μm, at least 15 μm, or at least 20 μm. In some embodiments, the first layer of fine fibers has an average mean flow pore size of up to 0.5 μm, up to 1 μm, up to 5 μm, up to 10 μm, up to 15 μm, up to 20 μm, up to 25 μm, up to 30 μm, or up to 35 μm. In an exemplary embodiment, the first layer of fine fibers has an average mean flow pore size in a range of 10 μm to 25 μm. In some embodiments, the average mean flow pore size is preferably determined using capillary flow porometry.

**[0129]** When the fibers of different diameters are layered, the effective pore size of the first layer of fine fibers will be dictated by the layer including the smallest fine fibers.

**[0130]** In some embodiments, the first layer of fine fibers has a basis weight of at least 0.005 g/m$^2$, at least 0.01 g/m$^2$, at least 0.05 g/m$^2$, at least 0.1 g/m$^2$, at least 0.5 g/m$^2$, at least 1 g/m$^2$, at least 1.5 g/m$^2$, at least 2 g/m$^2$, or at least 2.5 g/m$^2$. In some embodiments, the first layer of fine fibers has a basis weight of up to 1.5 g/m$^2$, up to 2 g/m$^2$, up to 2.5 g/m$^2$, up to 3 g/m$^2$, up to 3.5 g/m$^2$, up to 4 g/m$^2$, up to 4.5 g/m$^2$, up to 5 g/m$^2$, up to 10 g/m$^2$, up to 15 g/m$^2$, up to 20 g/m$^2$, up to 25 g/m$^2$, up to 50 g/m$^2$. In some embodiments, the first layer of fine fibers has a basis weight of at least 0.1 g/m$^2$ and up to 20 g/m$^2$. In another exemplary embodiment, the first layer of fine fibers has a basis weight of at least 0.1 g/m$^2$ and up to 1 g/m$^2$. In a further exemplary embodiment, the first layer of fine fibers has a basis weight 0.43 g/m$^2$. When the fibers of different diameters are layered, the basis weight of the first layer of fine fibers will be additive. Basis weight of the first layer of fine fibers may be from the mass of the first layer of fine fibers and the area of the scrim, according to the following equation: Basis weight of the first layer of fine fibers=(mass of the first layer of fine fibers)/(area of scrim). The mass of the fine fibers may be calculated from the polymer and spinning conditions used to make the fiber, according to the following equation: mass of fine fibers=(% w/v polymer in solution)×(pump rate)×(spinning time).

**[0131]** In some embodiments, the first layer of fine fibers has a solidity of at least 0.5%, at least 1%, at least 5%, at least 10%, at least 20%, at least 25%, at least 30%, or at least 40%. In some embodiments, the first layer of fine fibers has a solidity of up to 10%, up to 20%, up to 25%, up to 30%, up to 40%, or up to 50%. In an exemplary embodiment, the first layer of fine fibers has a solidity in a range of 0.5% to 30%. Solidity (c) of the first layer of fine fibers may be calculated from the dimensionless fiber drag parameter, F*1.0, using the following equation: $F^*_{1.0}=4.3548e^{8.8822c}$.

$F^*_{1.0}$ may be calculated from a modified Kirsch-Fuchs equation, as further described in the Examples.

**[0132]** In some embodiments, the first layer of fine fibers has a thickness of at least the average diameter of an average fine fiber of the first layer of fine fibers. In some embodiments, the first layer of fine fibers has a thickness of at least 0.2 μm, at least 0.3 μm, at least 0.4 μm, at least 0.5 μm, at least 0.6 μm, at least 0.7 μm, at least 0.8 μm, at least 0.9 μm, or at least 1 μm.

**[0133]** In some embodiments, the first layer of fine fibers has a thickness that is the thickness of several fibers having the average diameter of the first layer of fine fibers. For example, the first layer of fine fibers may have a thickness of at least 2 μm, at least 3 μm, at least 4 μm, or at least 5 μm.

**[0134]** In some embodiments, the first layer of fine fibers has a thickness of up to 1 μm, up to 5 μm, up to 10 μm, up to 30 μm, or up to 50 μm.

**[0135]** In some embodiments, the total thickness of the fine fiber layer may be measured using scanning electron microscopy (SEM). For example, a sample including at least the fine fiber layer and the support layer may be prepared for SEM by cross-sectioning the sample while frozen (for example, in liquid nitrogen). It may be useful to cross-section the sample while the sample is oriented with the support layer being cut before the fine fiber layer. It may further be useful to cross-section the sample while the sample is submerged in liquid nitrogen. An exemplary magnification that may be used is 1000×. It may be useful to use software to assist with the determination of sample thickness by allowing for outlining and re-shading of the fine fiber section in the SEM image. The re-shaded image may then be used to determine the maximal thickness of the fine fiber section in the image. In some embodiments, the total thickness of the fine fiber layer may be determining by averaging at least five maximal thicknesses from five separate images of the same sample.

Second Layer of Fine Fibers

**[0136]** The filter media described herein may include a second layer of fine fibers that is deposited on the first layer of fine fibers. In some embodiments, as further described herein, the filter media may additionally include a third layer of fine fibers, a fourth layer of fine fibers, etc.

**[0137]** As noted above, in some embodiments, the first layer of fine fibers includes fine fibers having an average diameter at least at least 3 times the average fiber diameter of a fiber of the second layer of fine fibers. In some embodiments, the first fiber layer includes fine fibers having an average diameter at least 3 times the average fiber diameter of the smallest fiber of the second fine fiber layer.

**[0138]** In some embodiments the smallest fibers of the second fine fiber layer have an average diameter of up to 0.3 μm, up to 0.4 μm, up to 0.5 μm, or up to 0.6 μm. In some embodiments, the average fiber diameter of the smallest fibers of the second fine fiber layer have an average diameter of at least 0.2 μm. For example, the average fiber diameter of the smallest fibers of the second fine fiber layer may be in a range of 0.2 μm to 0.6 μm, in a range of 0.3 μm to 0.5 μm, or in a range of 0.2 μm to 0.3 μm.

**[0139]** In some embodiments, the second layer of fine fibers may include a single layer including fibers having an average diameter at most one-third the average fiber diameter of the fibers of the first fine fiber layer (see, for example, FIG. **1**H).

**[0140]** In some embodiments, the second layer of fine fibers may include fine fibers of mixed diameters. For example, the second layer of fine fibers may include fine fibers of two different diameters (that is, small fine fibers and large fine fibers) (see FIG. **1**I and FIG. **1**J), wherein the large fine fibers have an average diameter at least 3 times the diameter of the small fine fibers.

**[0141]** In some embodiments the small fine fibers of the second fine fiber layer have an average diameter of up to 0.3 μm, up to 0.4 μm, up to 0.5 μm, or up to 0.6 μm. In some embodiments, the average fiber diameter of the small fine fibers of the second fine fiber layer have an average diameter of at least 0.2 μm. For example, the average fiber diameter of the small fine fibers of the second fine fiber layer may be in a range of 0.2 μm to 0.6 μm, in a range of 0.3 μm to 0.5 μm, or in a range of 0.2 μm to 0.3 μm.

**[0142]** In some embodiments, the large fine fibers of the second layer of fine fibers have an average fiber diameter of at least 1 μm, or greater than 1 μm. In some embodiments, the large fine fibers of the second layer of fine fibers have an average fiber diameter of up to 1 μm, up to 1.1 μm, up to 1.2 μm, up to 1.3 μm, up to 1.4 μm, up to 1.5 μm, up to 2 μm, up to 3 μm, up to 4 μm, up to 5 μm, or up to 10 μm.

**[0143]** Exemplary combinations of "large" fine fiber and "small" fine fiber diameters include, for example, 1 μm and 0.25 μm diameter fibers (see Examples 1-11); and 1.4 μm and 0.25 μm diameter fibers (see Example 12).

**[0144]** When the second layer of fine fibers includes both small fine fibers and large fine fibers, the fibers of mixed diameters may be commingled (as a result of having been formed simultaneously) (see FIG. **1**I), or layered (as a result of having been alternately applied to a substrate) (see FIG. **1**J and FIG. **1**L), or both (see FIG. **1**M). When the fibers of mixed diameters are layered (as a result of having been alternately applied to a substrate), then a single layer of fine fibers may include sub-layers of large fine fibers and small fine fibers.

**[0145]** The second layer of fine fibers may include any suitable mixture of fibers of mixed diameters. For example, when the second layer of fine fibers includes both small fine fibers and large fine fibers, the second layer of fine fibers may include at least 0.5% large fine fibers, at least 1% large fine fibers, at least 2% large fine fibers, at least 5% large fine fibers, at least 7% large fine fibers, at least 10% large fine fibers, at least 12% large fine fibers, at least 14% large fine fibers, at least 16% large fine fibers, at least 20% large fine fibers, at least 50% large fine fibers, at least 60% large fine fibers, at least 70% large fine fibers, or at least 80% large fine fibers. For example, when the second layer of fine fibers includes both small fine fibers and large fine fibers, the second layer of fine fibers may include up to 1% large fine fibers, up to 2% large fine fibers, up to 5% large fine fibers, up to 7% large fine fibers, up to 10% large fine fibers, up to 12% large fine fibers, up to 14% large fine fibers, up to 16% large fine fibers, up to 20% large fine fibers, up to 50% large fine fibers, up to 60% large fine fibers, up to 70% large fine fibers, up to 80% large fine fibers, or up to 90% large fine fibers. Some exemplary mixtures are shown in Table 1A-Table 1C. For example, the second layer of fine fibers may include the proportion of large fine fibers of one or more of Set A5, Set A6, Set B, Set D, Set D5, Set D6, Set E, Set I, Set I5, Set I6, Set J, or Set L of Table 1A-Table 1C.

**[0146]** In some embodiments, the proportion of large fine fibers is estimated from the diameters of small and large fine

fibers, % solids in precursor spinning solutions, syringe pump feed rates, and electrospinning time.

**[0147]** In some embodiments, the proportion of large fine fibers may be determined based on spin time using the equation provided in the Fiber Proportion Calculation section of the Examples.

**[0148]** In some embodiments, the proportion of large fine fibers may be determined by nano-computed tomography (nano-CT). For example, a sample of the filter media may be embedded in resin scanned as if slicing along the Z-axis. Useful images may be obtained by using, for example, a synchrotron-quality Nanoscale 3D X-ray Imaging machine such as Xradia 810 Ultra (Zeiss, Oberkochen, Germany). It may be useful to then stitch the images together, forming a 3D digital structure in order to use the digital structure to determine proportion of fibers having a particular diameter. The proportion of small/large fine fibers may be calculated by taking the ratio of the small/large fine fiber count against the total fiber (both small and large) count within the digital structure.

**[0149]** In some embodiments, the proportion of large fine fibers may be determined using microscopy. For example, sample images may be obtained via SEM at appropriate magnification (for example, 500×, 1000×, or 2500×). The presence of one or more fiber populations may be determined by counting all fibers within the image, followed by classifying into small fine fibers and large fine fibers based on grouping diameters within 25% variation. Fiber size may be measured and/or classified using image processing software such as ImageJ. The proportion of small/large fine fibers may be calculated by taking the ratio of the small/large fine fiber count against the total fiber (both small and large) count within the image.

**[0150]** For example, in an exemplary embodiment, the second layer of fine fibers may include at least 0.5% and up to 20% large fine fibers, more preferably, at least 1% and up to 10% large fine fibers, or, even more preferably, at least 5% and up to 7% large fine fibers. Additional ranges may also be useful including, for example, at least 3% and up to 9% large fine fibers, or at least 4% and up to 8% large fine fibers. Without wishing to be bound by theory, it is believed that optimizing the proportion of large fine fibers in the second layer of fine fibers provide support for the small fine fibers without disrupting the small fine fiber structure and resulting in a corresponding loss in efficiency.

**[0151]** In some embodiments, when the fibers of different diameters are layered, the second layer of fine fibers may include a sub-layer including large fine fibers deposited on a sub-layer including small fine fibers and/or a topmost sub-layer of large fine fibers (see FIG. **1**J-FIG. **1**M). Without wishing to be bound by theory, it is believed that including a topmost layer or sub-layer of a larger fine fibers may protect the previously deposited layers from blowing out and/or being damaged if a back-pulse cleaning (from the downstream side) is performed during the intended use of the filter media.

**[0152]** Any suitable combination of layers of small and large fine fibers may be used. Exemplary layered fiber structures that may be used for the second layer of fine fibers include one or more of Set A5, Set B, Set D5, Set E, Set I5, or Set J, of Table 1A-Table 1C. Exemplary commingled fiber structures that may be used for the second layer of fine fibers include one or more of Set A6, Set D, Set D6, Set I, or Set L, of Table 1A-Table 1C.

**[0153]** In some embodiments, both layered and commingled structures may be included in the second fine fiber layer. For example, as further described in Example 7, the second fine fiber layer may include a sub-layer of small fine fibers, then a sub-layer of commingled small fine fibers and large fine fibers, topped by a sub-layer of large fine fibers.

**[0154]** In some embodiments, the second layer of fine fibers has an average mean flow pore size of at least 0.1 μm, at least 0.5 μm, at least 1 μm, at least 5 μm, at least 10 μm, at least 15 μm, or at least 20 μm. In some embodiments, the first layer of fine fibers has an average mean flow pore size of up to 0.5 μm, up to 1 μm, up to 5 μm, up to 10 μm, up to 15 μm, up to 20 μm, up to 25 μm, up to 30 μm, or up to 35 μm. In an exemplary embodiment, the first layer of fine fibers has an average mean flow pore size in a range of 10 μm to 25 μm. In some embodiments, the average mean flow pore size is preferably determined using capillary flow porometry.

**[0155]** When the fibers of different diameters are layered, the effective pore size of the second layer of fine fibers will be dictated by the layer including the smallest fine fibers.

**[0156]** In some embodiments, the second layer of fine fibers has a basis weight of at least 0.005 $g/m^2$, at least 0.01 $g/m^2$, at least 0.05 $g/m^2$, at least 0.1 $g/m^2$, at least 0.5 $g/m^2$, at least 1 $g/m^2$, at least 1.5 $g/m^2$, at least 2 $g/m^2$, or at least 2.5 $g/m^2$. In some embodiments, the second layer of fine fibers has a basis weight of up to 1.5 $g/m^2$, up to 2 $g/m^2$, up to 2.5 $g/m^2$, up to 3 $g/m^2$, up to 3.5 $g/m^2$, up to 4 $g/m^2$, up to 4.5 $g/m^2$, up to 5 $g/m^2$, up to 10 $g/m^2$, up to 15 $g/m^2$, up to 20 $g/m^2$, up to 25 $g/m^2$, up to 50 $g/m^2$. In some embodiments, the second layer of fine fibers has a basis weight of at least 0.1 $g/m^2$ and up to 20 $g/m^2$. In another exemplary embodiment, second first layer of fine fibers has a basis weight of at least 0.1 $g/m^2$ and up to 1 $g/m^2$. In a further exemplary embodiment, the second layer of fine fibers has a basis weight 0.43 $g/m^2$. When the fibers of different diameters are layered, the basis weight of the second layer of fine fibers will be additive. Basis weight of the second layer of fine fibers may be from the mass of the second layer of fine fibers and the area of the scrim, according to the following equation: Basis weight of the second layer of fine fibers=(mass of the second layer of fine fibers)/(area of scrim). The mass of the second layer of fine fibers may be calculated from the polymer and spinning conditions used to make the fiber, according to the following equation: mass of fine fibers=(% w/v polymer in solution)×(pump rate)×(spinning time).

**[0157]** In some embodiments, the second layer of fine fibers has a solidity higher than the solidity of the first layer of fine fibers. That is, the first layer of fine fibers is preferably more open than the second layer of fine fibers. In some embodiments, the second layer of fine fibers has a solidity of at least 0.5%, at least 1%, at least 5%, at least 10%, at least 20%, at least 25%, at least 30%, or at least 40%. In some embodiments, the second layer of fine fibers has a solidity of up to 10%, up to 20%, up to 25%, up to 30%, up to 40%, or up to 50%. In an exemplary embodiment, the second layer of fine fibers has a solidity in a range of 0.5% to 30%. Solidity (c) of the second layer of fine fibers may be calculated from the dimensionless fiber drag parameter, F*1.0, using the following equation: $F^*_{1.0}=4.3548e^{8.8822c}$. $F^*_{1.0}$ may be calculated from a modified Kirsch-Fuchs equation, as further described in the Examples.

**[0158]** In some embodiments, the second layer of fine fibers has a thickness of at least the average diameter of an average fine fiber of the second layer of fine fibers. In some embodiments, the second layer of fine fibers has a thickness of at least 0.5 μm or at least 1 μm.

**[0159]** In some embodiments, the second layer of fine fibers has a thickness that is the thickness of several fibers having the average diameter of the second layer of fine fibers. For example, the second layer of fine fibers may have a thickness of at least 2 μm, at least 3 μm, at least 4 μm, or at least 5 μm.

**[0160]** In some embodiments, the second layer of fine fibers has a thickness of up to 5 μm, up to 10 μm, up to 30 μm, up to 40 μm, or up to 45 μm.

**[0161]** In some embodiments, the total thickness of the fine fiber layer may be measured using scanning electron microscopy (SEM). For example, a sample including at least the fine fiber layer and the support layer may be prepared for SEM by cross-sectioning the sample while frozen (for example, in liquid nitrogen). It may be useful to cross-section the sample while the sample is oriented with the support layer being cut before the fine fiber layer. It may further be useful to cross-section the sample while the sample is submerged in liquid nitrogen. An exemplary magnification that may be used is 1000×. It may be useful to use software to assist with the determination of sample thickness by allowing for outlining and re-shading of the fine fiber section in the SEM image. The re-shaded image may then be used to determine the maximal thickness of the fine fiber section in the image. In some embodiments, the total thickness of the fine fiber layer may be determining by averaging at least five maximal thicknesses from five separate images of the same sample.

**[0162]** In some embodiments, the over-all efficiency of the media may be directly related to the thickness of the second layer of fine fibers.

Properties of the Filter Media

**[0163]** As described above, the filter media includes a support layer and a layer of fine fibers. These layers may form a composite.

**[0164]** In some embodiments, the filter media has a composite average maximum pore size of up to 20 μm, preferably up to 15 μm, and more preferably up to 14 μm. In some embodiments, the composite average maximum pore size of the filter media is at least 0.1 μm. As used herein, "composite average maximum pore size" refers to the average maximum pore size of a composite that includes the support layer and the fine fiber layer.

**[0165]** In some embodiments, the filter media has a composite average mean flow pore size of up to 11 μm, preferably up to 9 μm, and more preferably up to 6 μm. In some embodiments, the composite average mean flow pore size of the filter media is at least 0.1 μm. As used herein, "composite average mean flow pore size" refers to the average mean flow pore size of a composite that includes the support layer and the fine fiber layer.

**[0166]** If the fine fiber layer includes multiple fine fiber layers, the composite includes each of the fine fiber layers.

**[0167]** In some embodiments, the composite average maximum pore size and/or composite average mean flow pore size are preferably determined using capillary flow porometry.

**[0168]** Without wishing to be bound by theory, it is believed that composite average maximum pore size and composite average mean flow pore size depends on the fine fiber diameters, relative amounts of small and large fine fibers, and composite morphology (such as layered or commingled), among other factors.

**[0169]** As described in Example 11, the composite average maximum pore size and/or the composite average mean flow pore size of the filter media may correlate with the ability of the filter media to withstand at least 20 psi pressure drop during liquid filtration, indicating better filter performance than a filter media that cannot withstand the same conditions.

Fine Fibers

**[0170]** The fine fibers of the present disclosure include a fiber-forming polymer material. In some embodiments, the fine fibers of the present disclosure may be made by spinning the fiber-forming polymer material alone. In some embodiments, the fine fibers of the present disclosure may be made by spinning the fiber-forming polymer material in combination with another sub stance.

**[0171]** Fine fiber technologies that contemplate polymeric materials mixed or blended with a variety of other substances is disclosed in Chung et al., U.S. Pat. No. 6,743,273; Chung et al., U.S. Pat. No. 6,924,028; Chung et al., U.S. Pat. No. 6,955,775; Chung et al., U.S. Pat. No. 7,070,640; Chung et al., U.S. Pat. No. 7,090,715; Chung et al., U.S. Patent Publication No. 2003/0106294; Barris et al., U.S. Pat. No. 6,800,117; and Gillingham et al., U.S. Pat. No. 6,673,136. Additionally, in Ferrer et al., U.S. Pat. No. 7,641,055, a water-insoluble, high-strength polymer material is made by mixing or blending a polysulfone polymer with a polyvinyl pyrrolidone polymer resulting in a single phase polymer alloy used in electrospinning fine fiber materials.

Fine Fibers Made from Polymer and Reactive Additives

**[0172]** In some embodiments, the fine fibers of the present disclosure may be made by combining a fiber-forming polymer material and at least two reactive additives that are capable of reacting with each other, for example, in a fiber-forming process or in a post-treatment process, as further described in International Patent Publication No. WO 2014/164130. The at least two reactive additives are optionally reactive with the fiber-forming polymer

**[0173]** In some embodiments, the fine fibers of the present disclosure may include at least one fiber-forming polymer; at least two reactive additives that are covalently bonded to each other and optionally covalently bonded to the fiber-forming polymer. In some embodiments, at least one of the reactive additives is self-condensed. In some embodiments, at least one of the reactive additives enhances at least one property of the fine fiber compared to the fine fiber without such reactive additive. "Enhancing" in this context means improving or creating one or more properties.

**[0174]** Reactive additives are selected such that they are preferably soluble in a solvent chosen for the polymer material for processing, such as in electrospinning.

**[0175]** In certain embodiments, the reactive additive is a monomer, oligomer, or small molecular weight polymer. For example, in certain embodiments, the reactive additive has a weight average molecular weight of less than 3000 Daltons. In certain embodiments, all of the reactive additives used to make the fine fibers have a weight average molecular weight of less than 3000 Daltons. In some embodiments, the

weight average molecular weight of the reactive additive may be determined using time of flight secondary ion mass spectrometry (TOF-SIMS).

**[0176]** Reactive additives can have a variety of reactive functional groups. For example, they can include alkoxy groups, hydroxyl groups, acid groups (for example, carboxylic acid groups), isocyanate groups, diglycidyl ether groups, dichloro groups. Any one molecule of a compound that functions as a reactive additive can include one or more of one type of functional group or two or more different functional groups. A reactive additive can include a mixture of compounds with differing numbers or types of functional groups. A hydroxyl-functional component can include a diol, a triol, a polyol, or a mixture thereof. A carboxylic acid-functional component can include a compound with multiple carboxylic acid groups (for example, a diacid, a triacid, or a mixture thereof). A glycidyl ether-functional component can include a compound with multiple glycidyl ether groups (for example, a diglycidyl ether, a triglycidyl ether, or a mixture thereof). An amine-functional component can include a primary amine compound, a secondary amine compound, a tertiary amine compound, or a mixture thereof. An amine-functional component can include a compound with multiple primary, secondary, or tertiary amine groups (for example, a diamine, a triamine, or a mixture thereof). An isocyanate-functional component can include a compound with multiple isocyanate groups (for example, a diisocyanate, a triisocyanate, or a mixture thereof). In addition, a reactive additive may have more than one type of reactive functional group. For example, citric acid and dimethylolpropionic acid have both hydroxyl and carboxylic acid groups.

**[0177]** In certain embodiments, at least one of the reactive additives is tri-functional or higher. By this it is meant, the reactive additive has three or more reactive functional groups per molecule. For example, 1,1,1-trimethylolpropane is a tri-functional alkoxy-containing compound; glycerol, pentaerythritol, erthitol, threitol, dipentaerythitol, sorbitol are multi-functional hydroxyl-containing reactive additives; citric acid and dimethylolpropionic acid are multi-functional carboxyl acid-containing reactive additives; trimethylolpropane triglycidyl ether is a tri-functional glycidyl ether-containing reactive additive; triphenylmethane triisocyanate is a tri-functional isocyanate-containing reactive additive; and triethylenetetramine, trimethylol propane, and tris(poly (propylene glycol) amine terminated) ether are multi-functional amine-containing reactive additives.

**[0178]** The following are examples of various reactive additives categorized by functional groups: (I) alkoxy-functional; (II) hydroxyl-functional; (III) acid-functional; (IV) glycidyl ether-functional; (V) isocyanate-functional; (VI) amine-functional; and (VII) dichloro-functional. Various reactive combinations (i.e., combinations of materials that are reactive with each other) can be used in making fine fibers of the present disclosure. For example, one or more reactive additives from Group (I) can be reacted one or more reactive additives from Group (II) and/or (III) and/or (IV) and/or (V) and/or (VI). One or more reactive additives from Group (II) can be reacted one or more reactive additives from Group (III) and/or (IV) and/or (V) and/or (VI) and/or (VII). One or more reactive additives from Group (III) can be reacted one or more reactive additives from Group (IV) and/or (V) and/or (VI) and/or (VII).

Fine Fibers Made from Polymer and Resinous Aldehyde Composition

**[0179]** In some embodiments, the fine fibers of the present disclosure may be made by combining a fiber-forming polymer material and a resinous aldehyde composition such as a melamine-formaldehyde resin.

**[0180]** In some embodiments, as further described below, the resinous aldehyde composition includes a "polymer-reactive resinous aldehyde composition." A "polymer-reactive resinous aldehyde composition" includes alkoxy groups, as further described in U.S. Pat. No. 9,587,328. In the final fibers, at least a portion of the polymer-reactive resinous aldehyde composition will be involved in crosslinking the polymer and optionally can be involved in self-crosslinking. The fiber-forming polymer material also includes reactive groups. In this context, "reactive" means that the polymer includes one or more functional groups (for example, active hydrogen groups) capable of being crosslinked by the alkoxy groups of the polymer-reactive resinous aldehyde composition used in making the fine fibers.

**[0181]** In some embodiments, as further described below, the resinous aldehyde composition includes a "polymer-non-reactive resinous aldehyde composition." The polymer-non-reactive resinous aldehyde composition includes reactive groups for self-crosslinking, as further described in U.S. Pat. No. 9,435,056. In the final fibers, at least portions of the polymer-non-reactive resinous aldehyde composition will be involved in self-crosslinking.

**[0182]** As used herein, "resin" or "resinous" refers to monomers, oligomers, and/or polymers, particularly of a nature that can migrate to the surface of a fine fiber during fiber formation. Herein, the term "resinous aldehyde composition" refers to the starting material as well as the material in the final fibers.

**[0183]** These components can be combined in solution or melt form. In certain embodiments, the fine fibers are electrospun from a solution or dispersion. Thus, the polymer materials and resinous aldehyde (for example, melamine-aldehyde) compositions are dispersible or soluble in at least one common solvent or solvent blend suitable for electrospinning.

Fine Fibers Made from Polymer Crosslinked with a Polymer-Reactive Resinous Aldehyde Composition

**[0184]** As further described in U.S. Pat. No. 9,587,328, in some embodiments, the fine fibers of the present disclosure may be made by combining a fiber-forming polymer material and a polymer-reactive resinous aldehyde composition that includes alkoxy groups, such as a reactive melamine-formaldehyde resin.

**[0185]** Referring to FIG. **9**A and FIG. **9**B, as the fiber **100**/**102** forms, the polymer-reactive resinous aldehyde composition preferably forms at least one exterior concentric (coaxial) layer (that is, phase), such as a second coating phase **22** (fiber **102**, FIG. **9**B) comprising predominantly the polymer-reactive resinous aldehyde composition (for example, melamine-aldehyde composition), or two exterior concentric layers (that is, phases) such as a second coating phase **20** (fiber **100**, FIG. **9**A) comprising a mixture of the polymer material and a polymer-reactive resinous aldehyde composition, and a third exterior phase (outermost phase) **30** (FIG. **9**A) comprising predominantly the polymer-reactive resinous aldehyde composition. That is, the polymer-reactive resinous aldehyde composition may migrate to the surface to form a two-phase fiber (FIG. **9**B) or a three-phase

fiber (FIG. **9**A), in which the core **10** (FIG. **9**A) or **12** (FIG. **9**B) comprises primarily the polymer material (for example, nylon). Generally, the more polymer-reactive resinous aldehyde content relative to polymer, the greater the tendency to form a three-phase fiber.

**[0186]** In some embodiments, the fine fiber of the present disclosure may preferably be prepared from a polymer-reactive resinous aldehyde composition comprising alkoxy groups and a polymer comprising active hydrogen groups, wherein the molar ratio of polymer-reactive resinous aldehyde composition to polymer is such that the molar ratio of alkoxy groups of the polymer-reactive resinous aldehyde composition to active hydrogen groups of the polymer is greater than 5:100, greater than 10:100, greater than 20:100, greater than 40:100, or greater than 60:100. In some embodiments, the molar ratio of polymer-reactive resinous aldehyde composition to polymer may be such that the molar ratio of alkoxy groups in the polymer-reactive resinous aldehyde composition to active hydrogen groups in the polymer is no greater than 300:100, no greater than 250:100, or no greater than 210:100).

**[0187]** In certain embodiments, a weight ratio of polymer-reactive resinous aldehyde composition to polymer of greater than 5:100, greater than 10:100, greater than 20:100, greater than 40:100, or greater than 60:100 may be used. In some embodiments, the weight ratio may be used to control the formation of a useful exterior phase including the polymer-reactive resinous aldehyde composition surrounding the core polymer. The exterior coating layer of predominantly polymer-reactive resinous aldehyde composition (for example, melamine-formaldehyde) provides improved properties, such as humidity resistance, to the fine fibers and fine fiber layers of the disclosure, relative to commercially available fibers and fiber layers. In this context, "predominantly" means the referenced material is present in a particular region (for example, coating, layer, or phase) in a major amount (that is, greater than 50% by weight) of the material in that region.

**[0188]** For example, in an exemplary embodiment, the weight ratio of the polymer-reactive resinous aldehyde composition to polymer may be in a range of 5:100 to 300:100. In another exemplary embodiment, the weight ratio of the polymer-reactive resinous aldehyde composition to polymer may be in a range of 20:100 to 100:100.

**[0189]** Suitable polymer-reactive resinous aldehyde compositions include two or more alkoxy groups per molecule that are capable of crosslinking a polymer used in making the fine fibers as described herein. Exemplary polymer-reactive resinous aldehyde compositions are synthetic resins made by treating various aldehydes with a reactant under condensation reaction conditions. Useful such reactants include phenol, urea, aniline, benzoguanamine, glycoluril, and melamine. Useful polymer-reactive resinous aldehyde compositions include aldehyde-based agents that may be used in crosslinking reactions. The polymer-reactive resinous aldehyde compositions are typically nonvolatile. The polymer-reactive resinous aldehyde compositions (when combined with polymers such as nylon, as described in greater detail below) should also be soluble in a solvent chosen for the polymer material for processing, such as in electrospinning. Polymer-reactive resinous aldehyde compositions useful as crosslinking agents include a condensation product of urea and an aldehyde, a condensation product of phenol and an aldehyde, or a condensation product of melamine and an aldehyde. One useful class of crosslinking resins includes resins based on nitrogen compounds such as melamine, urea, benzoguanamine, glycoluril, and other similar resins manufactured by reacting an aldehyde with a nitrogen compound. Such amine-based crosslinking resins are soluble in process solvents and possess reactivity with a variety of polymer species.

**[0190]** Useful polymer-reactive resinous aldehyde compositions (for example, melamine-aldehyde compositions) include crosslinking agents, and optionally other nonreactive room-temperature-stable resin components, that may be combined in solution or melt form with a variety of polymer materials. Melamine forms resinous compositions with a variety of other co-reactants.

**[0191]** Useful melamine-aldehyde compositions include melamine-aldehyde products generally formed by the reaction between melamine and an aldehyde compound. Useful aldehyde compounds include $C_{1-6}$ alkanals including formaldehyde, acetaldehyde, butyraldehyde, isobutyraldehyde, and the like. Mixtures of such aldehydes may be used if desired. The melamine-aldehyde resins, and other suitable polymer-reactive resinous aldehyde compositions, include components having at least two alkoxy groups per molecule. Typical partially and fully reacted melamine-aldehydes have from 3 to 6, or from 4 to 6, alkoxy groups per molecule.

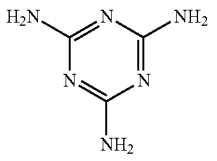
**[0192]** In certain embodiments, the polymer-reactive resinous aldehyde composition comprises a condensation product of urea and an aldehyde, a condensation product of phenol and an aldehyde, a condensation product of melamine and an aldehyde, or a mixture thereof. In certain embodiments, the polymer-reactive resinous aldehyde composition comprises a condensation product of benzoguanamine and an aldehyde, a condensation product of glycouril and an aldehyde, or a mixture thereof.

**[0193]** Useful polymer-reactive resinous aldehyde compositions (for example, melamine-aldehyde compositions) include compounds and mixtures thereof including: highly methylated melamine; partially methylated melamine; methylated high imino melamine; highly alkylated mixed ether melamine; highly alkylated carboxylated, high imino mixed ether melamine; highly n-butylated melamine; n-butylated high imino and partially n-butylated melamine; partially iso-butylated melamine; partially n-butylated urea; partially iso-butylated urea; glycoluril; highly alkylated mixed ether melamine-formaldehyde; highly alkylated mixed ether carboxylated melamine resin; hexa butoxy methyl melamine; butoxy methyl melamine; highly alkylated mixed ether melamine; methoxymethyl methylol melamine, highly methylated melamine resins; melamine-formaldehyde resin co-etherified with methanol and n-butoxy ethanol/n-butanol blend; melamine-formaldehyde resin co-etherified with methanol and n-butanol in n-butanol; butylated melamine-formaldehyde resin dissolved in a blend of n-butanol and butyl glycol; hexa butoxy methyl melamine; partially n-butylated melamine; high solids, highly methylated melamine resins; various polymer-reactive resinous aldehyde compositions sold under the trade names CYMEL available from Cytec Industries of West Paterson, N.J., wherein such compositions include, for example, CYMEL 301, CYMEL 303 LF, CYMEL 350, CYMEL 3745, CYMEL MM-100, CYMEL 370, CYMEL 373, CYMEL 3749, CYMEL 323, CYMEL 325, CYMEL 327, CYMEL 328, CYMEL 385, CYMEL 481, CYMEL 1116, CYMEL 1130, CYMEL 1133, CYMEL 1135, CYMEL 1161, CYMEL 1168, CYMEL

1125, CYMEL 1141, CYMEL 202, CYMEL 203, CYMEL 254, CYMEL 1156, CYMEL 1158, CYMEL 9370, CYMEL MB-98, CYMEL MB-11-B, CYMEL MB-14-B, CYMEL 615, CYMEL 651, CYMEL 683, CYMEL 688, CYMEL MI-12-I, CYMEL MI-97-IX, CYMEL UM-15, CYMEL U-80, CYMEL UB-24-BX, CYMEL UB-25-BE, CYMEL UB-26-BX, CYMEL UB-30-B, CYMEL UB-90-BX, CYMEL U-227-8, CYMEL U-610, CYMEL U-640, CYMEL U-646, CYMEL U-662, CYMEL U-663, CYMEL U-665, CYMEL UI-19-I, CYMEL UI-19-IE, CYMEL UI-20-E, CYMEL UI-38-I, CYMEL 1123, CYMEL 659, CYMEL 1172, CYMEL 1170, and the like; and various polymer-reactive resinous aldehyde compositions sold under the trade name LUWIPAL and available from the BASF AG of Ludwigshafen, Germany, wherein such compositions include, for example, LUWIPAL LR 8955, LUWIPAL LR 8968, and LUWIPAL LR 8984. Such resins are also available from INEOS Melamines Inc., and sold under the trade names RESIMENE (for example, RESIMENE HM 2608), MAPRENAL, and MADURIT. Various combinations of polymer-reactive resinous aldehyde compositions may be used if desired.

**[0194]** In an exemplary embodiment, a melamine-formaldehyde resin (sometimes referred to herein as simply a "melamine composition" or "melamine resin") is used. Reference to melamine-formaldehyde resins means a melamine-based resin that has two or more (at least two) alkoxy functional groups (methoxy, ethoxy, propoxy, butoxy, etc.) per melamine molecule. Besides the alkoxy functional groups, the melamine-formaldehyde resins may have NH, hydroxyl, or carboxylic acid functional groups. Uncrosslinked melamine-formaldehyde is a thermosetting plastic (thermoset) additive used for crosslinking polymers that strengthens the crosslinked polymer as it is heated. Once set, it cannot be remolded or set to form a different shape. Crosslinked melamine-formaldehyde plastics retain their strength and shape, unlike other types of thermoplastics that soften with heat and harden when cooled (such as acetate, acrylic, and nylon). Crosslinked melamine-formaldehyde is stain-resistant and resistant to strong solvents and water. Depending on the functional groups in the melamine-formaldehyde resins, uncrosslinked resins may be both water soluble and water insoluble, or soluble in organic solvents such as alcohols, hydrocarbons (toluene, xylene, etc.) or others, or a mixture of these solvents.

**[0195]** Melamine-formaldehyde resins are made from the reaction of formaldehyde with melamine. Melamine (chemical formula $C_3H_6N_6$) and formaldehyde (chemical formula $CH_2O$) have the following structures:

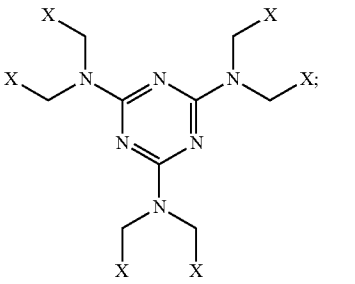


Melamine

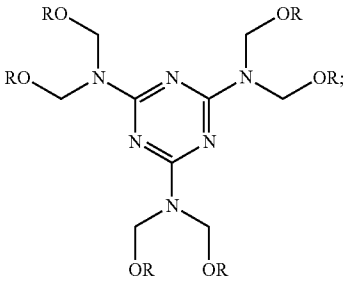


Formaldehyde

wherein melamine is 1,3,5-triazine-2,4,6-triamine; or 2,4,6-triamino-s-triazine; or cyanuro triamide. Representative structures for the melamine-formaldehyde resin are shown in structure I or II:



I



II

wherein in compound I, X is H or alkoxy or hydroxyl and at least two X groups are alkoxy. Preferably, if the compound has two or three alkoxy groups, the alkoxy groups are not on the same nitrogen substituent. The melamine resin compound I needs at a minimum two reactive or crosslinkable alkoxy groups. Representative compound II is a fully reacted compound referred to as a hexa(alkoxymethyl)melamine type resin, wherein R is H or alkyl (methyl, ethyl, butyl, etc.) (such that OR is an alkoxy group (methoxy, ethoxy, butoxy, etc.)).

**[0196]** Melamine resins are part of a larger class of amino resins. They are used as bonding agents in plywood and particle board and wrinkle-resistance agents in textiles. They are also molded for electrical devices and various commercial and home applications. They are also used as crosslinkers in paper towels to increase water resistance. When we refer to melamine-formaldehyde resins we refer to uncrosslinked melamine resins. It is sold under various trade names, including CYMEL, LUWIPAL, RESIMENE, MAPRENAL, etc.

**[0197]** An exemplary such melamine resin is hexa(methoxymethyl)melamine (HMMM) (for example, structure II above wherein R is methyl). As reaction partners for HMMM, polymers having active hydrogen groups, predominantly amide, hydroxyl, carboxyl or anhydride functional groups, have been used for making films.

**[0198]** If desired, and depending on the polymer-reactive resinous aldehyde composition, for example, the crosslinking reaction described herein may need a strong acid catalyst such as a sulfonic acid, such as para-toluene sulfonic acid. In certain embodiments, a catalyst such as an acid catalyst is preferably used in an amount of at least 4 wt-%, based on polymer solids, to enhance crosslinking speed. Typically, no more than 10 wt-% catalyst, such as an acid catalyst, is used in the crosslinking reaction of the present disclosure.

**[0199]** If desired, fine fibers formed from the crosslinking reaction between a polymer-reactive resinous aldehyde composition and a polymer material, as described herein, may be enhanced, for example, with respect to speed and extent of

crosslinking, by exposing the fine fibers to thermal treatment. Such thermal treatment typically includes a temperature of at least 80° C., at least 100° C., or at least 120° C., and typically no greater than 150° C., for typically at least 5 seconds, and typically no greater than 10 minutes.

**[0200]** In the fibers of the disclosure, the polymer-reactive resinous aldehyde composition of the disclosure is combined with a polymer material that comprises a polymer or polymer mixture or blend. The polymer or polymer mixture or blend is selected such that it may be combined with the polymer-reactive resinous aldehyde composition in a solution or dispersion or in the melt. The combination of polymer material and polymer-reactive resinous aldehyde composition, in certain embodiments, should be substantially stable in the melt or in solution or dispersion form for sufficient time such that the fiber may be formed.

**[0201]** The polymer or polymer mixture or blend should include at least one fiber-forming polymer that includes one or more active hydrogen groups capable of being crosslinked by the polymer-reactive resinous aldehyde composition. Preferred such polymer materials include one or more active hydrogen groups capable of reacting with and crosslinking to the polymer-reactive resinous aldehyde compositions. Active hydrogen groups include, but are not limited to, thiol (—SH), hydroxyl (—OH), carboxylate (—$CO_2H$), amido (—C(O)—NH— or —C(O)—$NH_2$), amino (—$NH_2$), or imino (—NH—), and anhydride (—$COO)_2R$ groups (upon hydrolysis). These groups may be found in pendent polymer groups or in the polymer backbone.

**[0202]** Polymer materials suitable for use in the polymeric compositions of the disclosure include both addition polymer and condensation polymer materials with active hydrogens. Suitable examples include poly(meth)acrylic acids, polyamides, cellulose ethers and esters, poly(maleic anhydride), polyamines such as chitosan and mixtures, blends, alloys, and block, graft, or random copolymers thereof. Such copolymers may include one or more other moieties in addition to those listed in the previous sentence. Preferred materials that fall within these generic classes include poly (vinyl alcohol) in various degrees of hydrolysis (for example, 87% to 99.5%) in crosslinked and non-crosslinked forms. Preferred addition polymers tend to be glassy, that is, having a $T_g$ (glass transition temperature) greater than room temperature. Additionally, polymer materials that have low crystallinity, such as poly(vinyl alcohol) materials, are also useful as the polymer materials of the disclosure.

**[0203]** Other preferred examples of useful polymer materials include cellulose derivatives selected from the group consisting of ethyl cellulose, hydroxyl ethyl cellulose, cellulose acetate, cellulose acetate butyrate, cellulose acetate propionate, cellulose acetate phthalate, and mixtures thereof; poly(meth)acrylic acid homopolymers and copolymers, including for example, styrene-(meth)acrylic acid copolymers and ethylene-(meth)acrylic acid copolymers; polyvinyl alcohol homopolymers or copolymers, including for example, a polyvinyl butyral and an ethylene co-vinyl alcohol copolymer; poly(maleic anhydride) homopolymers or copolymers, including for example, a styrene-maleic anhydride copolymer; and polyurethanes. Herein, a poly (meth)acrylic acid refers to poly(acrylic acid) and poly (methacrylic acid) polymers.

**[0204]** Many types of polyamides are also useful as the polymer materials in the fibers of the disclosure. One useful class of polyamide condensation polymers are nylon materials. The term "nylon" is a generic name for all long chain synthetic polyamides. Typically, nylon nomenclature includes a series of numbers such as in nylon-6,6 which indicates that the starting materials are a $C_6$ diamine and a $C_6$ diacid (the first digit indicating a $C_6$ diamine and the second digit indicating a $C_6$ dicarboxylic acid compound). Another nylon may be made by the polycondensation of ε-caprolactam in the presence of a small amount of water. This reaction forms a nylon-6 (made from a cyclic lactam, also known as ε-aminocaproic acid) that is a linear polyamide. Further, nylon copolymers are also contemplated. Exemplary nylon materials include nylon-6, nylon-6,6, nylon-6,10, mixtures or copolymers thereof.

**[0205]** Copolymers may be made by combining various diamine compounds, various diacid compounds and various cyclic lactam structures in a reaction mixture and then forming the nylon with randomly positioned monomeric materials in a polyamide structure. For example, a nylon-6, 6-6,10 material is a nylon manufactured from hexamethylene diamine and a $C_6$ and a $C_{10}$ blend of diacids. A nylon-6-6,6-6,10 is a nylon manufactured by copolymerization of ε-aminocaproic acid, hexamethylene diamine and a blend of a $C_6$ and a $C_{10}$ diacid material. Herein, the term "copolymer" includes polymers made from two or more different monomers and include terpolymers, etc.

**[0206]** Block copolymers are also useful as the polymer materials in the fibers of the disclosure. With such copolymers, where fibers will be electrospun, the choice of solvent or solvent blend is important. The selected solvent or solvent blend is selected such that both blocks are soluble in the solvent. Examples of useful block copolymers include PEBAX ε-caprolactam-b-ethylene oxide, available from Arkema Inc. of Philadelphia, Pa.; and polyurethanes of ethylene oxide and isocyanates.

**[0207]** Addition polymers like polyvinyl alcohol, and amorphous addition polymers such as poly(acrylonitrile) copolymers with acrylic acid are also useful. They may be solution spun with relative ease because they are soluble or dispersible in a variety of solvents and solvent blends at low pressures and temperatures. A poly(vinyl alcohol) having a hydrolysis degree of, for example, from 87% to 99.9+% may be used as the polymer material in the fibers of the disclosure.

**[0208]** Preferred polymers within this embodiment include a polyamides (particularly nylon), polyester amides, a polyvinyl alcohol, an ethylene-co-vinyl alcohol polymer, a polyvinyl butyral, and poly(maleic anhydride), polyvinyl pyrrolidone and its copolymers. Preferred active hydrogen groups include hydroxyl, amino, and amido groups. Various combinations of polymer materials may be used if desired.

**[0209]** Optionally, in addition to the polymers with reactive hydrogen groups, the polymer material used in the fibers of the disclosure may include one or more nonreactive polymers. In this context, "nonreactive" is defined as being unable to crosslink with melamine-formaldehyde resins or other polymer-reactive resinous aldehyde composition used. For example, polymer materials such as many polyolefins, polyvinyl chloride, chlorinated polyethylene and other such materials may be used, wherein such polymers have no groups that may crosslink with the polymer-reactive resinous aldehyde composition. Other nonreactive polymers include polyacetals, polyesters (both aromatic based and aliphatic, including, for example, poly(ethylene terephthalate) (PET), polybutylene terephthalate (PBT), polycapro-

lactone (PCL), poly-L-lactic acid (PLLA), poly D-lactic acid (PLDA), etc.), polyester-co-polyethylene oxide, polyalkylene sulfides, polyarylene oxides (including, for example, polyphenylene oxide), polysulfones, modified polysulfones (including, for example, polyethersulfone), poly(vinylpyridine) (including, for example, poly(4-vinylpyridine), poly (2-vinylpyridine) and random and block copolymers therefore (including, for example, styrene vinyl pyridine, vinyl pyridine-co-butyl methacrylate, vinyl pyridine-co-methyl methacrylate. etc.)), polyvinyl acetate and its copolymers (including, for example, ethylene-co-vinyl acetate) and the like. Preferred materials that fall within these generic classes include polyethylene, polypropylene, poly(vinyl chloride), acrylic resins including poly(methylmethacrylate), polystyrene and copolymers (including both random and block copolymers such as ABA type block copolymers) thereof (including, for example, styrene acrylonitrile (SAN), styrene maleic anhydride (SMA), styrene-co-vinyl pyridine, styrene-co-butadiene, styrene-co-ethylene propylene, styrene-co-methyl methacrylate, styrene-co-ethyl methacrylate, styrene-co-butyl methacrylate, styrene-co-methyl acrylate, styrene-co-ethyl acrylate, styrene-co-butyl acrylate etc.), poly(vinylidene fluoride) and its copolymers (including, for example, PVDF-co-HFP), poly(vinylidene chloride), mixtures, blends, or alloys. Examples of useful block copolymers include ABA-type copolymers (for example, styrene-EP-styrene) (wherein "EP" refers to ethylene-propylene) or AB (for example, styrene-EP) polymers, KRATON styrene-b-butadiene and styrene-b-hydrogenated butadiene(ethylene propylene), available from Kraton Polymers U.S. LLC of Houston, Tex.; and SYMPATEX polyester-b-ethylene oxide, available from SympaTex Technologies Inc. of Hampton, N.H. Various combinations of nonreactive polymers may be used if desired.

**[0210]** If desired, a nonreactive polymer may be used in an amount that does not adversely impact the positive effects of the crosslinking that occurs upon use of a polymer having active hydrogens.

**[0211]** Addition nonreactive polymers like poly(vinylidene fluoride), syndiotactic polystyrene, copolymers of vinylidene fluoride and hexafluoropropylene, polyvinyl acetate, amorphous addition polymers such as polystyrene, poly(vinyl chloride) and its various copolymers, and poly (methyl methacrylate) and its various copolymers may be solution spun with relative ease because they are soluble or dispersible in a variety of solvents and solvent blends at low pressures and temperatures. However, highly crystalline polymers like polyethylene and polypropylene typically require high temperature, high pressure solvents or solvent blends if they are to be solution spun. Therefore, solution spinning of the polyethylene and polypropylene is very difficult.

Fine Fibers Made from Polymer Crosslinked with a Polymer-Non-Reactive Resinous Aldehyde Composition

**[0212]** As further described in U.S. Pat. No. 9,435,056, in some embodiments, the fine fibers of the present disclosure may be made by combining a fiber-forming polymer material and a polymer-non-reactive resinous aldehyde composition that includes reactive groups for self-crosslinking.

**[0213]** Referring to FIG. **10**A and FIG. **10**B, as the fiber **200**/**202** forms, the polymer-non-reactive resinous aldehyde composition preferably forms at least one exterior concentric layer (i.e., phase), such as a second coating phase **222** (fiber **202**, FIG. **10**B) comprising predominantly the polymer-non-reactive resinous aldehyde composition (for example, melamine-aldehyde composition), or two exterior concentric layers (i.e., phases) such as a second coating phase **220** (fiber **200**, FIG. **10**A) comprising a mixture of the polymer material and a polymer-non-reactive resinous aldehyde composition, and a third exterior phase (outermost phase) **230** (FIG. **10**A) comprising predominantly the polymer-non-reactive resinous aldehyde composition. That is, the polymer-non-reactive resinous aldehyde composition can migrate to the surface to form a two-phase fiber (FIG. **10**B) or a three-phase fiber (FIG. **10**A), in which the core **210** (fiber **200**) or **212** (FIG. **10**B) comprises primarily the polymer material (for example, poly(4-vinyl pyridine) also referred to as P4VP).

**[0214]** In this context, "predominantly" means the referenced material is present in a particular region (for example, coating, layer, or phase) in a major amount (that is, greater than 50% by weight) of the material in that region.

**[0215]** Preferably, the fine fiber of the present disclosure is prepared from a self-crosslinkable polymer-non-reactive resinous aldehyde composition comprising reactive groups (preferably, alkoxy groups) and a polymer comprising no, or a low amount of, reactive groups (that is, groups capable of reacting with the reactive groups of the polymer-non-reactive resinous aldehyde composition), wherein the weight ratio of self-crosslinkable polymer-non-reactive resinous aldehyde to nonreactive polymer is greater than 5:100, greater than 10:100, greater than 20:100, greater than 40:100, or greater than 60:100.

**[0216]** In some embodiments, the weight ratio of the self-crosslinkable polymer-non-reactive resinous aldehyde composition to nonreactive polymer is no greater than 300:100, no greater than 250:100, no greater than 210:100, or no greater than 100:100.

**[0217]** For example, in an exemplary embodiment, the weight ratio of the self-crosslinkable polymer-non-reactive resinous aldehyde composition to nonreactive polymer may be in a range of 5:100 to 300:100. In another exemplary embodiment, the weight ratio of the self-crosslinkable polymer-non-reactive resinous aldehyde composition to nonreactive polymer may be in a range of 20:100 to 100:100.

**[0218]** In some embodiments, the weight ratio may be used to control the formation of polymer/semi-interpenetrating network type structure wherein the interpenetrating network is the self-crosslinked polymer-non-reactive resinous aldehyde. This structure may provide improved properties, such as humidity resistance, to the fine fibers and fine fiber layers of the invention.

**[0219]** Suitable polymer-non-reactive resinous aldehyde compositions include one or more reactive groups that are capable of self-crosslinking in a fiber-making process as described herein. Such reactive groups include alkoxy groups as well as hydroxyl, carboxylic acid, and/or —NH groups. Exemplary polymer-non-reactive resinous aldehyde compositions are synthetic resins made by treating various aldehydes with a reactant under condensation reaction conditions. Useful such reactants include phenol, urea, aniline, benzoguanamine, glycoluril, and melamine. Useful polymer-non-reactive resinous aldehyde compositions include aldehyde-based agents that can be used in self-crosslinking reactions. The resinous aldehyde compositions are typically nonvolatile. The polymer-non-reactive resinous aldehyde compositions should also be soluble in a solvent chosen for the polymer material for processing, such as in electrospin-

ning. Resinous aldehyde compositions useful as crosslinking agents include, a condensation product of urea and an aldehyde, a condensation product of phenol and an aldehyde, or a condensation product of melamine and an aldehyde. One useful class of crosslinking resins includes resins based on nitrogen compounds such as melamine, urea, benzoguanamine, glycoluril, and other similar resins manufactured by reacting an aldehyde with a nitrogen compound. Such self-crosslinking resins are soluble in process solvents and possess reactivity with a variety of polymer species.

**[0220]** Useful polymer-non-reactive resinous aldehyde compositions (for example, melamine-aldehyde compositions) include crosslinking agents, and optionally other nonreactive room-temperature-stable resin components, that can be combined in solution or melt form with a variety of polymer materials. Melamine forms resinous compositions with a variety of other co-reactants.

**[0221]** Useful melamine-aldehyde compositions include melamine-aldehyde products generally formed by the reaction between melamine and an aldehyde compound. Useful aldehyde compounds include $C_{1-6}$ alkanals including formaldehyde, acetaldehyde, butyraldehyde, isobutyraldehyde, and the like. Mixtures of such aldehydes can be used if desired. The melamine-aldehyde resins, and other suitable resinous aldehyde compositions, include components having at least two alkoxy groups per molecule. Typical partially and fully reacted melamine-aldehydes have from 3 to 6, or from 4 to 6, alkoxy groups per molecule.

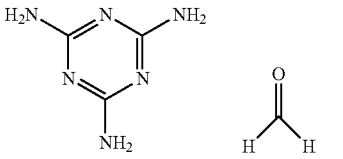
**[0222]** In certain embodiments, the polymer-non-reactive resinous aldehyde composition comprises a condensation product of urea and an aldehyde, a condensation product of phenol and an aldehyde, a condensation product of melamine and an aldehyde, or a mixture thereof. In certain embodiments, the polymer-non-reactive resinous aldehyde composition comprises a condensation product of benzoguanamine and an aldehyde, a condensation product of glycouril and an aldehyde, or a mixture thereof.

**[0223]** Useful polymer-non-reactive resinous aldehyde compositions (for example, melamine-aldehyde compositions) include compounds and mixtures thereof including: partially methylated melamine; methylated high imino melamine; high imino mixed ether melamine; n-butylated high imino and partially n-butylated melamine; partially iso-butylated melamine; partially n-butylated urea; partially iso-butylated urea; glycoluril; methoxymethyl methylol melamine resins; among others that self-crosslink.

**[0224]** Various melamine compositions that self-crosslink are sold under the trade names CYMEL available from Cytec Industries of West Paterson, N.J., wherein such compositions include, for example, CYMEL 3745, CYMEL MM-100, CYMEL 3749, CYMEL 323, CYMEL 325, CYMEL 327, CYMEL 328, CYMEL 370, CYMEL 373, CYMEL 385, CYMEL 1158, CYMEL 1172, CYMEL UM-15, CYMEL U-64, CYMEL U-65, CYMEL U-21-571, CYMEL U-93-210, CYMEL U-216-10-LF, CYMEL U-227-8, CYMEL U-1050-10, CYMEL U-1052-8, CYMEL U-1054, CYMEL UB-25-BE, CYMEL UB-30-B, CYMEL U-662, CYMEL U-663, CYMEL U-1051, CYMEL UI-19-1, CYMEL UI-21E, CYMEL UI-27-EI, CYMEL UI-38-I, and the like; and various melamine compositions sold under the trade name LUWIPAL and available from the BASF AG of Ludwigshafen, Germany, wherein such compositions include, for example, LUWIPAL LR 8955, LUWIPAL LR 8968, and LUWIPAL LR 8984. Such resins are also available from INEOS Melamines Inc. sold under the trade names RESIMENE (for example, RESIMENE HM2608), MAPRENAL, and MADURIT. The primary condition for such material is the ability of it to self-condense (i.e., self-crosslink). Various combinations of polymer-non-reactive resinous aldehyde compositions can be used if desired; however, such combinations will include at least one self-crosslinking polymer-non-reactive aldehyde component.

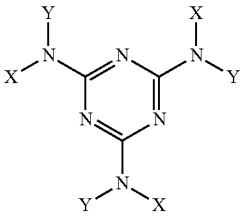
**[0225]** In many preferred embodiments, a melamine-formaldehyde resin (sometimes referred to herein as simply a "melamine" composition or "melamine" resin) is used. Reference to melamine-formaldehyde resins means a melamine-based resin that has two or more (at least two) alkoxy functional groups (methoxy, ethoxy, propoxy, butoxy, etc.) per melamine molecule. Besides the alkoxy functional groups, the melamine-formaldehyde resins include imine (—NH—), carboxylic acid (—C(O)OH), or hydroxyl (—OH) functional groups, or combinations thereof, to impart the ability to self-crosslink. Depending on the functional groups in the melamine formaldehyde resins, uncrosslinked resins can be both water soluble and water insoluble, or soluble in organic solvents such as alcohols, hydrocarbons (toluene, xylene, etc.) or others, or a mixture of these solvents.

**[0226]** Melamine-formaldehyde resins are made from the reaction of formaldehyde with melamine. Melamine (chemical formula $C_3H_6N_6$) and formaldehyde (chemical formula $CH_2O$) have the following structures:



Melamine Formaldehyde

wherein melamine is 1,3,5-triazine-2,4,6-triamine; or 2,4,6-triamino-s-triazine; or cyanuro triamide. A representative structure for the melamine-formaldehyde resin is shown in structure I:



wherein in compound I, each X and each Y is independently H, —$(CH_2)_x$—O—R (R═H or ($C_1$-$C_4$)alkyl and x=1-4), or —$(CH_2)_y$—C(O)OH (y=1-4), and further wherein at least two of the X and Y groups are —$(CH_2)_x$—O—R (R═($C_1$-$C_4$)alkyl and x=1-4), and at least one of the X and Y groups is H, —$(CH_2)_x$—OH (x=1-4), and/or —$(CH_2)_y$—C(O)OH (y=1-4). Preferably if the compound has two or three —$(CH_2)_x$—O—R (R═$C_1$-$C_4$ alkyl and x=1-4) groups, they are not on the same nitrogen substituent.

**[0227]** In the fibers of the disclosure, the self-crosslinkable polymer-non-reactive resinous aldehyde composition of the disclosure is combined with a polymer material that comprises a polymer or polymer mixture or blend. The polymer or polymer mixture or blend is selected such that it can be combined with the polymer-non-reactive resinous aldehyde composition in a solution or dispersion or in the melt. The combination of polymer material and polymer-non-reactive resinous aldehyde composition, in certain embodiments, should be substantially stable in the melt or in solution or dispersion form for sufficient time such that the fiber can be formed.

**[0228]** The polymer or polymer mixture or blend should include at least one fiber-forming polymer, and should include no, or very few, reactive groups capable of being crosslinked by the polymer-non-reactive resinous aldehyde composition. Exemplary polymer reactive groups that should not be present include active hydrogen groups. Active hydrogen groups include, but are not limited to thiol (—SH), hydroxyl (—OH), carboxylate (—$CO_2H$), amido (—C(O)—NH— or —C(O)—$NH_2$), amino (—$NH_2$), or imino (—NH—), and anhydride (—$COO)_2R$ groups (upon hydrolysis).

Polymer materials suitable for use in the polymeric compositions of the disclosure include both addition polymer and condensation polymer materials that are nonreactive polymers. In this context, "nonreactive" is defined as being unable to crosslink with the polymer-non-reactive resinous aldehyde composition used (as compared to reactive polymers (for example nylon) as described above and in U.S. Pat. No. 9,587,328. For example, polymer materials such as many polyolefins, polyvinyl chloride, chlorinated polyethylene and other such materials may be used, wherein such polymers have no groups that may crosslink with the polymer-reactive resinous aldehyde composition. Other nonreactive polymers include polyacetals, polyesters (both aromatic based and aliphatic, including, for example, poly (ethylene terephthalate) (PET), polybutylene terephthalate (PBT), polycaprolactone (PCL), poly-L-lactic acid (PLLA), poly D-lactic acid (PLDA), etc.), polyester-co-polyethylene oxide, polyalkylene sulfides, polyarylene oxides (including, for example, polyphenylene oxide), polysulfones, modified polysulfones (including, for example, polyethersulfone), poly(vinylpyridine) (including, for example, poly(4-vinylpyridine), poly(2-vinylpyridine) and random and block copolymers therefore (including, for example, styrene vinyl pyridine, vinyl pyridine-co-butyl methacrylate, vinyl pyridine-co-methyl methacrylate. etc.)), polyvinyl acetate and its copolymers (including, for example, ethylene-co-vinyl acetate) and the like. Preferred materials that fall within these generic classes include polyethylene, polypropylene, poly(vinyl chloride), acrylic resins including poly(methylmethacrylate), polystyrene and copolymers (including both random and block copolymers such as ABA type block copolymers) thereof (including, for example, styrene acrylonitrile (SAN), styrene maleic anhydride (SMA), styrene-co-vinyl pyridine, styrene-co-butadiene, styrene-co-ethylene propylene, styrene-co-methyl methacrylate, styrene-co-ethyl methacrylate, styrene-co-butyl methacrylate, styrene-co-methyl acrylate, styrene-co-ethyl acrylate, styrene-co-butyl acrylate etc.), poly(vinylidene fluoride) and its copolymers (including, for example, PVDF-co-HFP), poly (vinylidene chloride), mixtures, blends, or alloys. Examples of useful block copolymers include ABA-type copolymers (for example, styrene-EP-styrene) (wherein "EP" refers to ethylene-propylene) or AB (for example, styrene-EP) polymers, KRATON styrene-b-butadiene and styrene-b-hydrogenated butadiene(ethylene propylene), available from Kraton Polymers U.S. LLC of Houston, Tex.; and SYMPATEX polyester-b-ethylene oxide, available from SympaTex Technologies Inc. of Hampton, N.H. Various combinations of nonreactive polymers may be used if desired.

**[0229]** Addition nonreactive polymers like poly(vinylidene fluoride), syndiotactic polystyrene, copolymers of vinylidene fluoride and hexafluoropropylene, polyvinyl acetate, amorphous addition polymers such as polystyrene, poly(vinyl chloride) and its various copolymers, and poly (methyl methacrylate) and its various copolymers can be solution spun with relative ease because they are soluble or dispersible in a variety of solvents and solvent blends at low pressures and temperatures. However, highly crystalline polymers like polyethylene and polypropylene typically require high temperature, high pressure solvents or solvent blends if they are to be solution spun. Therefore, solution spinning of the polyethylene and polypropylene is very difficult.

**[0230]** If desired, and depending on the polymer-non-reactive resinous aldehyde composition, for example, the self-crosslinking reaction described herein may need a strong acid catalyst such as a sulfonic acid, such as para-toluene sulfonic acid. In certain embodiments, a catalyst such as an acid catalyst is preferably used in an amount of at least 4 wt-%, based on polymer solids, to enhance self-crosslinking speed. Typically, no more than 10 wt-% catalyst, such as an acid catalyst, is used in the self-crosslinking reaction of the present disclosure.

Methods of Making

**[0231]** In another aspect, this disclosure describes a method of making the fine fiber layers and the support layer.

**[0232]** The fine fiber layers may be formed by any suitable method. Fine fibers of the disclosure may be made using a variety of techniques including electrostatic spinning, force spinning, wet spinning, dry spinning, melt spinning, extrusion spinning, direct spinning, gel spinning, etc.

**[0233]** In some embodiments, the first fine fiber layer is preferably formed on the support layer.

**[0234]** The fine fibers are collected on the support layer during, for example, electrostatic or melt spinning formation, and are often heat treated after fiber making. Preferably, the first layer of fine fibers is disposed on a first surface of a layer of permeable coarse fibrous media (that is, a support layer) as a layer of fiber.

Methods of Making the Fibers

**[0235]** In a fiber spinning process for making fine fibers of the disclosure, the polymer being spun is typically converted into a fluid state (for example, by dissolution in solvent or melting). The fluid polymer is then forced through the spinneret, where the polymer cools to a rubbery state, and then a solidified state. The aldehyde composition may migrate to the surface as the fluid polymer transitions to a solid state. Wet spinning is typically used for polymers that need to be dissolved in a solvent to be spun. The spinneret is submerged in a chemical bath that causes the fiber to precipitate, and then solidify, as it emerges. The process gets its name from this "wet" bath. Acrylic, rayon, aramid,

modacrylic, and spandex are produced via this process. Dry spinning is also used for polymers that are dissolved in solvent. It differs in that the solidification is achieved through evaporation of the solvent. This evaporation is usually achieved by a stream of air or inert gas. Because there is no precipitating liquid involved, the fiber does not need to be dried, and the solvent is more easily recovered. Melt spinning is used for polymers that may be melted. The polymer solidifies by cooling after being extruded from the spinneret.

**[0236]** In a typical process, pellets or granules of the solid polymer are fed into an extruder. The pellets are compressed, heated and melted by an extrusion screw, then fed to a spinning pump and into the spinneret. A direct spinning process avoids the stage of solid polymer pellets. The polymer melt is produced from the raw materials, and then from the polymer finisher directly pumped to the spinning mill. Direct spinning is mainly applied during production of polyester fibers and filaments and is dedicated to high production capacity (greater than 100 tons/day). Gel spinning, also known as dry-wet spinning, is used to obtain high strength or other special properties in the fibers. The polymer is in a "gel" state, only partially liquid, which keeps the polymer chains somewhat bound together. These bonds produce strong inter-chain forces in the fiber, which increase its tensile strength. The polymer chains within the fibers also have a large degree of orientation, which increases strength. The fibers are first air dried, then cooled further in a liquid bath. Some high strength polyethylene and aramid fibers are produced via this process.

**[0237]** An alternative for making fine fibers of the disclosure is a melt-blowing process. Melt-blowing (also referred to herein as "MB") is a process for producing fibrous webs or articles directly from polymers or resins using high-velocity air or another appropriate force to attenuate the filaments. This process is unique because it is used almost exclusively to produce microfibers rather than fibers the size of normal textile fibers. MB microfibers generally have diameters in the range of 2 to 4 μm (micrometers or microns or μ), although they may be as small as 0.1 μm and as large as 10 to 15 μm. Differences between MB nonwoven fabrics and other nonwoven fabrics, such as degree of softness, cover or opacity, and porosity may generally be traced to differences in filament size. As soon as the molten polymer is extruded from the die holes, high velocity hot air streams (exiting from the top and bottom sides of the die nosepiece) attenuate the polymer streams to form microfibers. As the hot air stream containing the microfibers progresses toward the collector screen, it entrains a large amount of surrounding air (also called secondary air) that cools and solidifies the fibers. The solidified fibers subsequently get laid randomly onto the collecting screen, forming a self-bonded nonwoven web. The fibers are generally laid randomly (and also highly entangled) because of the turbulence in the air stream, but there is a small bias in the machine direction due to some directionality imparted by the moving collector. The collector speed and the collector distance from the die nosepiece may be varied to produce a variety of melt-blown webs. Usually, a vacuum is applied to the inside of the collector screen to withdraw the hot air and enhance the fiber laying process.

**[0238]** Any of the above-listed processes for making the fine fiber of the disclosure may be used to make the permeable coarse fibrous material for the support layer. Spunbond techniques may also be used for making the permeable coarse fibrous material for the support layer. Spunbond fabrics are produced by depositing extruded, spun filaments onto a collecting belt in a uniform random manner followed by bonding the fibers. The fibers are separated during the web laying process by air jets or electrostatic charges. The collecting surface is usually perforated to prevent the air stream from deflecting and carrying the fibers in an uncontrolled manner. Bonding imparts strength and integrity to the web by applying heated rolls or hot needles to partially melt the polymer and fuse the fibers together. Since molecular orientation increases the melting point, fibers that are not highly drawn may be used as thermal binding fibers. Polyethylene or random ethylene-propylene copolymers are used as low melting bonding sites. Spunbond products are employed in carpet backing, geotextiles, and disposable medical/hygiene products. Since the fabric production is combined with fiber production, the process is generally more economical than when using staple fiber to make nonwoven fabrics. The spinning process is similar to the production of continuous filament yarns and utilizes similar extruder conditions for a given polymer. Fibers are formed as the molten polymer exits the spinnerets and is quenched by cool air. The objective of the process is to produce a wide web and, therefore, many spinnerets are placed side by side to generate sufficient fibers across the total width. The grouping of spinnerets is often called a block or bank. In commercial production two or more blocks are used in tandem in order to increase the coverage of fibers.

**[0239]** In a spunbond process, before deposition on a moving belt or screen, the output of a spinneret usually consists of a hundred or more individual filaments which must be attenuated to orient molecular chains within the fibers to increase fiber strength and decrease extensibility. This is accomplished by rapidly stretching the plastic fibers immediately after exiting the spinneret. In practice the fibers are accelerated either mechanically or pneumatically. In most processes the fibers are pneumatically accelerated in multiple filament bundles; however, other arrangements have been described where a linearly aligned row or rows of individual filaments is pneumatically accelerated.

**[0240]** In a traditional textile spunbond process some orientation of fibers is achieved by winding the filaments at a rate of approximately 3,200 m/min to produce partially oriented yarns (POY). The POYs may be mechanically drawn in a separate step for enhancing strength. In spunbond production filament bundles are partially oriented by pneumatic acceleration speeds of 6,000 m/min or higher. Such high speeds result in partial orientation and high rates of web formation, particularly for lightweight structures (for example, 17 $g/m^2$). The formation of wide webs at high speeds is a highly productive operation.

**[0241]** For many applications, partial orientation of the course fibers of the support layer sufficiently increases strength and decreases extensibility to give a functional fabric (for example, a diaper cover stock). However, some applications, such as primary carpet backing, require filaments with very high tensile strength and low degree of extension. For such application, the filaments are drawn over heated rolls with a typical draw ratio of 3.5:1. The filaments are then pneumatically accelerated onto a moving belt or screen. This process is slower, but gives stronger webs.

**[0242]** The spunbond web is formed by the pneumatic deposition of the filament bundles onto the moving belt. A pneumatic gun uses high-pressure air to move the filaments through a constricted area of lower pressure, but higher velocity as in a venturi tube. For the web to achieve maximum uniformity and cover, individual filaments may be separated before reaching the belt. This separation is accomplished by inducing an electrostatic charge onto the bundle while under tension and before deposition. The charge may be induced triboelectrically or by applying a high voltage charge. The former is a result of rubbing the filaments against a grounded, conductive surface. The electrostatic charge on the filaments may be at least 30,000 electrostatic units per square meter (esu/$m^2$).

**[0243]** Fine fibers of the disclosure may preferably be made using an electrostatic spinning process. A suitable electrospinning apparatus for forming the fine fibers includes a reservoir in which the fine fiber forming solution is contained, and an emitting device, which generally consists of a rotating portion including a plurality of offset holes. As it rotates in the electrostatic field, a droplet of the solution on the emitting device is accelerated by the electrostatic field toward the collecting media. Facing the emitter, but spaced apart therefrom, is a grid upon which the collecting media (that is, a substrate or combined substrate) is positioned. Air may be drawn through the grid. A high voltage electrostatic potential is maintained between emitter and grid by means of a suitable electrostatic voltage source. The substrate is positioned in between the emitter and grid to collect the fiber.

**[0244]** Specifically, the electrostatic potential between grid and the emitter imparts a charge to the material which cause liquid to be emitted therefrom as thin fibers which are drawn toward grid where they arrive and are collected on substrate. In the case of the polymer in solution, a portion of the solvent is evaporated off the fibers during their flight to the substrate. The fine fibers bond to the substrate fibers as the solvent continues to evaporate. Electrostatic field strength is selected to ensure that as the polymer material is accelerated from the emitter to the collecting media, the acceleration is sufficient to render the polymer material into a very thin microfiber or nanofiber structure. Time of deposition may be used to control the number of emitted fibers deposited on the forming media, thereby allowing control of the thickness of each layer deposited thereon. Electrospinning processes usually use polymer solutions with 5% to 20% solids (on polymer) concentration. Solvents that are safe and easy to use are desired in industrial applications. On the other hand, fibers formed with such solvents often need to survive and perform in a wide variety of environments.

Methods of Making a Layer of Fine Fibers Including Single Diameter Fibers

**[0245]** In another aspect, this disclosure describes making a layer of fine fibers deposited on a support layer. As further described above, the layer of fine fibers may include a single (or first) layer of fine fibers that includes both large fine fibers having an average diameter at least 3 times the average fiber diameter of smaller fine fibers or the layer of fine fibers may include at least two layers of fine fibers where the first layer of fine fibers includes fine fibers having an average diameter at least 3 times the average fiber diameter of the smallest fibers of the second fine fiber layer. This section describes a method of making a layer of fine fibers including a first fine fiber layer including a single diameter fine fiber. The following section describes making a layer of fine fibers that includes both large fine fibers having an average diameter at least 3 times the average fiber diameter of smaller fine fibers in the same layer (for example, the first fine fiber layer or the second fine fiber layer).

**[0246]** A suitable polymer and polymer concentration may be selected by a person having ordinary skill in the art given the size and other properties desired for the first layer of fine fibers. For example, in some embodiments, the fibers will preferably be compatible with a fluid (for example, hydraulic fluid, fuel, lubricant) they are used to filter. A fiber is considered to be compatible with a fluid if it does not react with the fluid or any other components and additives in it and is insoluble in the fluid (such that the fine fiber structure is not chemically nor physically compromised upon mere contact with the fluid). In an exemplary embodiment, the polymer solution includes Solution 2 or Solution 4, as described in the Examples.

Methods of Making a Layer of Fine Fibers Including Mixed Diameter Fine Fibers

**[0247]** In a further aspect, this disclosure describes making a layer of fine fibers that includes a layer of fine fibers that includes both large fine fibers having an average diameter at least 3 times the average fiber diameter of smaller fine fibers in the same layer. Such a layer may be deposited directly on the support layer (that is, the first fine fiber layer) or it may be deposited on a first fine fiber layer (that is, the second fine fiber layer), or both. In addition, a layer of fine fibers that includes both large fine fibers having an average diameter at least 3 times the average fiber diameter of smaller fine fibers in the same layer may form a third fine fiber layer, a fourth fine fiber layer, etc.

**[0248]** A suitable polymer and polymer concentration may be selected by a person having ordinary skill in the art given the size and other properties desired for the second layer of fine fibers. For example, in some embodiments, the fibers will preferably be compatible with a fluid (for example, hydraulic fluid, fuel, lubricant) they are used to filter. A fiber is considered to be compatible with a fluid if it does not react with the fluid or any other components and additives in it and is insoluble in the fluid (such that the fine fiber structure is not chemically nor physically compromised upon mere contact with the fluid). In an exemplary embodiment, the polymer solution includes Solution 1 Solution 2, Solution 3, and/or Solution 4, as described in the Examples.

**[0249]** In some embodiments when the fine fibers of different diameters are commingled, the fibers may be formed at the same time. For example, when two (or more) fibers are formed by electrospinning, the fibers may be formed by simultaneously co-spinning including, for example, by using two (or more) syringes, wherein each syringe includes a different polymer solution. Additionally or alternatively, each syringe may use a different syringe pump feed rate. In some embodiments, when the fine fibers of different diameters are commingled, the fibers may be formed alternating formation of the fibers but using very short (for example, up to 10 seconds, up to 20 seconds, or up to 30 seconds) pulses of each polymer solution.

**[0250]** In some embodiments when the fibers of different diameters are layered, the fibers may be formed by alternating formation of the fibers. For example, when two (or

more) fibers are formed by electrospinning, the fibers may be formed by alternatively spinning each fiber including, for example, by using two (or more) syringes, wherein each syringe includes a different polymer solution. Additionally or alternatively, each syringe may use a different syringe pump feed rate. In some embodiments, when the fibers of different diameters are layered, the fibers may be formed alternating formation of the fibers using pulses of each polymer solution of at least 30 seconds.

**[0251]** Any suitable method may be used to form a combination of layers of small and large fine fibers may be used. Exemplary methods that may be used to form layered fiber structures include one or more of the methods of Set A5, Set B, Set D5, Set E, Set I5, or Set J, of Table 1A-Table 1C. Exemplary methods that may be used to form commingled fiber structures include one or more of the methods of Set A6, Set D, Set D6, Set I, or Set L, of Table 1A-Table 1C. In some embodiments, a combination of layers that includes both layered fiber structures and commingled fiber structures may be formed. An exemplary method for forming such a structure is described in Example 7.

Methods of Using and Filter Elements

**[0252]** In some embodiments, the filter media disclosed herein may be included in a filter element that includes a wire support. The wire support may be located downstream of the support layer.

**[0253]** In some embodiments, the filter media, including, for example, a filter media encompassed in a filter element, may be pleated.

**[0254]** The filter media of the present disclosure may be manufactured into filter elements, including flat-panel filters, cartridge filters, or other filtration components. Examples of such filter elements are described in U.S. Pat. Nos. 6,746,517; 6,673,136; 6,800,117; 6,875,256; 6,716,274; and 7,316,723.

**[0255]** In some embodiments, the filter element may include an efficiency layer, and the efficiency layer may include the filter media disclosed herein. That is, the filter media described herein may form the efficiency layer or may form a portion of the efficiency layer. In some embodiments, the filter element may further comprise a loading layer. Any suitable media may be used as a loading layer including, for example, a meltblown nonwoven layer or another media designed to act as a depth-loading layer.

**[0256]** In some embodiments, the filter media of the present disclosure may be used to filer a fluid including, for example a fluid stream. Fluids include air, gas, and liquids. In some embodiments, the filter media of the present disclosure may be used to remove particulate from a fluid stream.

**[0257]** In some embodiments, the filter media of the present disclosure may be used to filter air. In some embodiments, including when the filter media of the present disclosure is used to filter air, the filter media may be located upstream of other layers in the filter element.

**[0258]** In some embodiments, the filter media of the present disclosure may be used to filter a gas. Gaseous streams can include, for example, air and/or industrial waste gasses. In an exemplary embodiment, the filter media of the present disclosure may be used to filter blow-by gases from the crankcase of diesel engines, which carry substantial amounts of entrained oils therein, as aerosol. In a further exemplary embodiment, the filter media of the present disclosure may be used in a gas turbine.

**[0259]** In some embodiments, the filter media of the present disclosure may be used to filter a liquid. In some embodiments, including when the filter media of the present disclosure is used to filter a liquid, the filter media may be located downstream of other layers in the filter element. Exemplary liquids may include, for example, an aqueous liquid, hydraulic fluid, oil, fuel, a lubricant, etc. Aqueous liquids may include natural and man-made streams such as effluents, cooling water, process water, etc.

**[0260]** In some exemplary embodiments, the filter media disclosed herein may replace the efficiency layer in a filter element of WO 2015/157638; WO 2016/210153; WO 2018/208819; U.S. Pat. Nos. 7,160,451; 7,238,285; 7,988,860; 8,263,214; 8,834,610; 8,673,040; or U.S. Pat. No. 8,721,756.

**[0261]** In some embodiments, the filter medium of the present disclosure may be used in an application in which flow rate varies including, for example, in a hydraulic application. Variations in flow rate including, for example, cyclic flow conditions, have an adverse effect of filter media performance and, in particular, on filter media efficiency because variations in flow rate result in a particle having multiple opportunities to pass through a media opening.

**[0262]** At the time of the invention, the effect of varying flow rates on filter media performance was typically minimized by increasing efficiency of the filter media, but increasing the efficiency of the filter media also resulted in a corresponding increase in pressure drop—that is, an increase in the pressure necessary to force fluid through the filter media. Such an increase in pressure drop results in more opportunities for the filter to be bypassed (for example, via a bypass valve), increases energy consumption, and shortens filter life. In contrast, the filter medium of the present disclosure can achieve increased efficiency under cyclic flow conditions without compromising pressure drop.

**[0263]** Additional exemplary embodiments of filter elements including the filter media described herein and methods of making and using those filter elements, particularly under cyclic flow conditions, are provided in co-pending application entitled FILTER MEDIUM COMPRISING A FINE FIBER LAYER, Attorney Docket No. 0444.000106WO01, filed on even date herewith.

**[0264]** The invention is defined in the claims. However, below there is provided a non-exhaustive listing of non-limiting exemplary aspects. Any one or more of the features of these aspects may be combined with any one or more features of another example, embodiment, or aspect described herein.

Exemplary Filtration Media Aspects Including at Least One Fine Fiber Layer

**[0265]** Aspect A1 is a filtration media comprising: a support layer; a first layer of fine fibers, wherein the first layer of fine fibers is deposited on the support layer, and wherein the first layer of fine fibers comprises large fine fibers and small fine fibers, the large fine fibers having an average diameter of at least 3 times the average diameter of the small fine fibers.

**[0266]** Aspect A2 is the filtration media of Aspect A1, wherein the large fine fibers of the first layer of fine fibers have an average diameter of at least 1 μm, or greater than 1 μm; or wherein the large fine fibers of the first layer of fine

fibers have an average diameter of up to 1.1 μm, up to 1.2 μm, up to 1.3 μm, up to 1.4 μm, up to 1.5 μm, up to 2 μm, up to 3 μm, up to 4 μm, up to 5 μm, or up to 10 μm; or both.

**[0267]** Aspect A3 the filtration media of Aspect A1 or A2, wherein the first layer of fine fibers comprises small fine fibers, wherein small fine fibers have an average diameter of at least 0.2 μm; or wherein the small fine fibers have an average diameter of up to 0.3 μm, up to 0.4 μm, up to 0.5 μm, or up to 0.6 μm; or both.

**[0268]** Aspect A4 is the filtration media of any one of the preceding Aspects, wherein the first layer of fine fibers comprises up to 10% large fine fibers or up to 20% large fine fibers.

**[0269]** Aspect A5 is the filtration media of one of the preceding Aspects, wherein the first layer of fine fibers comprises at least 3% and up to 9% large fine fibers, at least 5% and up to 7% large fine fibers, or at least 4% and up to 8% large fine fibers.

**[0270]** Aspect A6 is the filtration media of any one of the preceding Aspects, wherein the first layer of fine fibers comprises the proportion of large fine fibers of one or more of Set A5, Set A6, Set B, Set D, Set D5, Set D6, Set E, Set I, Set I5, Set I6, Set J, or Set L of Table 1A-Table 1C.

**[0271]** Aspect A7 is the filtration media of any one of Aspects A1 to A6, wherein the proportion of the large fine fibers is determined based on spin time.

**[0272]** Aspect A8 is the filtration media of any one of Aspects A1 to A6, wherein the proportion of the large fine fibers is determined using microscopy or nano-CT.

**[0273]** Aspect A9 is the filtration media of any one of the preceding Aspects, wherein the first layer of fine fibers comprises a layered fiber structure.

**[0274]** Aspect A10 is the filtration media of Aspect A9, wherein the first layer of fine fibers comprises the layered fiber structure of one or more of Set A5, Set B, Set D5, Set E, Set I5, or Set J, of Table 1A-Table 1C.

**[0275]** Aspect A11 is the filtration media of Aspect A9, wherein the first layer of fine fibers comprises small fine fibers and large fine fibers, and wherein within the first layer of fine fibers, the small fine fibers are deposited on a first sub-layer of large fine fibers and a second sub-layer of large fine fibers are deposited on the small fine fibers.

**[0276]** Aspect A12 is the filtration media of any one of Aspects A1 to A8, wherein the first layer of fine fibers comprises a commingled fiber structure.

**[0277]** Aspect A13 is the filtration media of Aspect A12, wherein the first layer of fine fibers comprises the commingled fiber structure of one or more of Set A6, Set D, Set D6, Set I, or Set L, of Table 1A-Table 1C.

**[0278]** Aspect A14 is the filtration media of any one of the preceding Aspects, wherein the filtration media further comprises a second fine fiber layer.

**[0279]** Aspect A15 is the filtration media of any one of the preceding Aspects, wherein the fine fibers are compatible with at least one of a hydraulic fluid, fuel, or lubricant.

**[0280]** Aspect A16 is the filtration media of any one of the preceding Aspects, wherein the support layer comprises nylon.

**[0281]** Aspect A17 is the filtration media of any one of the preceding Aspects, wherein the support layer has an average mean flow pore size of at least 5 μm, at least 10 μm, at least 15 μm, at least 20 μm, or at least 25 μm and up to 10 μm, up to 15 μm, up to 20 μm, up to 25 μm, up to 30 μm, up to 35 μm, up to 40 μm, up to 50 μm, up to 60 μm, up to 70 μm, up to 80 μm, or up to 90 μm.

**[0282]** Aspect A18 is the filtration media of Aspect A17, wherein the average mean flow pore size is determined using capillary flow porometry.

**[0283]** Aspect A19 is the filtration media of any one of the preceding Aspects, wherein the support layer has an average maximum pore size of up to 10 μm, up to 15 μm, up to 20 μm, up to 25 μm, up to 30 μm, up to 35 μm, up to 40 μm, up to 50 μm, up to 60 μm, up to 70 μm, up to 80 μm, up to 90 μm, up to 100 μm, or up to 150 μm.

**[0284]** Aspect A20 is the filtration media of Aspect A19, wherein the average maximum pore size is determined using capillary flow porometry.

**[0285]** Aspect A21 is the filtration media of any one of the preceding Aspects, wherein the support layer has an average minimum pore size of at least 5 μm, at least 10 μm, at least 15 μm, at least 20 μm, at least 25 μm, at least 30 μm, at least 35 μm, at least 40 μm, or at least 50 μm.

**[0286]** Aspect A22 is the filtration media of Aspect A21, wherein the average minimum pore size is determined using capillary flow porometry.

**[0287]** Aspect A23 is the filtration media of any one of the preceding Aspects, wherein the support layer has an average mean flow pore size, and wherein the average mean flow pore size of the support layer does not vary by more than 30%, does not vary by more than 25%, or does not vary by more than 15% across the length and width of the media.

**[0288]** Aspect A24 is the filtration media of any one of the preceding Aspects, wherein the filtration media comprises a composite comprising the support layer and the fine fiber layer; wherein the filtration media has a composite average maximum pore size of up to 14 μm, up to 15 μm, or up to 20 μm; or wherein the filtration media has a composite average maximum pore size of at least 0.1 μm; or both; wherein Aspect A25 is the filtration media of any one of the preceding Aspects, wherein the filtration media comprises a composite comprising the support layer and the fine fiber layer; wherein the filtration media has a composite average mean flow pore size of up to 11 μm, up to 9 μm, or up to 6 μm; or wherein the filtration media has a composite average mean flow pore size of at least 0.1 μm; or both.

**[0289]** Aspect A26 is the filtration media of Aspect A24 or A25, wherein the composite pore size is determined using capillary flow porometry.

**[0290]** Aspect A27 is the filtration media of any one of the preceding Aspects, wherein the large fine fibers have a diameter at least 0.2 μm, at least 0.3 μm, or at least 0.4 μm greater than a diameter of the small fine fibers.

**[0291]** Aspect A28 is the filtration media of any one of the preceding Aspects, wherein the first fine fiber layer may have a thickness of at least 2 μm, at least 3 μm, at least 4 μm, or at least 5 μm; or wherein the first fine fiber layer may have a thickness of up to 5 μm, up to 10 μm, up to 30 μm, or up to 50 μm; or both.

**[0292]** Aspect A29 is the filtration media of Aspect A28, wherein the thickness of the fine fiber layer is determined using scanning electron microscopy (SEM).

**[0293]** Aspect A30 is the filtration media of any one of the preceding Aspects, wherein the support layer comprises a spunbond layer.

**[0294]** Aspect A31 is a filter element comprising the filtration media of any one of the preceding Aspects.

**[0295]** Aspect A32 is the filter element of Aspect A31, wherein the filter element comprises an efficiency layer, and the efficiency layer comprises the filtration media.

**[0296]** Aspect A33 is the filter element of Aspect A32, wherein the filter element further comprises a loading layer.

Exemplary Filtration Media Aspects Including at Least Two Fine Fiber Layers

**[0297]** Aspect B1 is a filtration media comprising: a support layer; a first layer of fine fibers and a second layer of fine fibers; wherein the first layer of fine fibers is deposited on the support layer and comprises fibers having an average diameter at least 3 times the average fiber diameter of a fine fiber of the second fine fiber layer; and wherein the second layer of fine fibers is deposited on the first layer of fibers.

**[0298]** Aspect B2 is the filtration media of Aspect B1, wherein the fine fibers of the first layer of fine fibers have an average diameter of greater than 0.6 μm, at least 0.7 μm, at least 0.8 μm, at least 0.8 μm, at least 1 μm, or greater than 1 μm; or wherein the fine fibers of the first layer of fine fibers have an average diameter of up to 1.1 μm, up to 1.2 μm, up to 1.3 μm, up to 1.4 μm, up to 1.5 μm, up to 2 μm, up to 3 μm, up to 4 μm, up to 5 μm, or up to 10 μm; or both.

**[0299]** Aspect B3 is the filtration media of Aspect 1 or 2, wherein the second layer of fine fibers comprises fine fibers of mixed diameters.

**[0300]** Aspect B4 is the filtration media of Aspect B3, wherein the second layer of fine fibers comprises large fine fibers and small fine fibers, the large fine fibers having an average diameter of at least 3 times the average diameter of the small fine fibers of the second layer of fine fibers.

**[0301]** Aspect B5 is the filtration media of Aspect B3 or B4, wherein the second layer of fine fibers comprises large fine fibers and small fine fibers, wherein the large fine fibers have an average diameter of at least 1 μm or greater than 1 μm; or wherein the large fine fibers have an average diameter of to 1.1 μm, up to 1.2 μm, up to 1.3 μm, up to 1.4 μm, up to 1.5 μm, up to 2 μm, up to 3 μm, up to 4 μm, up to 5 μm, or up to 10 μm; or both; and wherein the small fine fibers have an average diameter of at least 0.2 μm; or wherein the small fine fibers have an average diameter of up to 0.6 μm; or both.

**[0302]** Aspect B6 is the filtration media of Aspect B4 or B5, wherein the large fine fibers have an average diameter of greater than 1 μm.

**[0303]** Aspect B7 is the filtration media of any one of Aspects B4 to B6, wherein the second layer of fine fibers comprises up to 10% large fine fibers or up to 20% large fine fibers.

**[0304]** Aspect B8 is the filtration media of any one of Aspects B4 to B7, wherein the second layer of fine fibers comprises at least 3% and up to 9% large fine fibers, at least 5% and up to 7% large fine fibers, or at least 4% and up to 8% large fine fibers.

**[0305]** Aspect B9 is the filtration media of any one of Aspects B4 to B6, wherein the second layer of fine fibers comprises the proportion of large fine fibers of one or more of Set A5, Set A6, Set B, Set D, Set D5, Set D6, Set E, Set I, Set I5, Set I6, Set J, or Set L of Table 1A-Table 1C.

**[0306]** Aspect B10 is the filtration media of any one of Aspects B7 to B9, wherein the proportion of the large fine fibers is determined based on spin time.

**[0307]** Aspect B11 is the filtration media of any one of Aspects B7 to B9, wherein the proportion of the large fine fibers is determined using microscopy or nano-CT.

**[0308]** Aspect B12 is the filtration media of any one of Aspects B3 to B11, wherein the second layer of fine fibers comprises a layered fiber structure.

**[0309]** Aspect B13 is the filtration media of Aspect B12, wherein the second layer of fine fibers comprises the layered fiber structure of one or more of Set A5, Set B, Set D5, Set E, Set 15, or Set J, of Table 1A-Table 1C.

**[0310]** Aspect B14 is the filtration media of Aspect B12, wherein the second layer of fine fibers comprises small fine fibers and large fine fibers, and wherein within the second layer of fine fibers, the small fine fibers are deposited on a first sub-layer of large fine fibers and a second sub-layer of large fine fibers are deposited on the small fine fibers.

**[0311]** Aspect B15 is the filtration media of any one of Aspects B3 to B11, wherein the second layer of fine fibers comprises a commingled fiber structure.

**[0312]** Aspect B16 is the filtration media of Aspect B15, wherein the second layer of fine fibers comprises the commingled fiber structure of one or more of Set A6, Set D, Set D6, Set I, or Set L, of Table 1A-Table 1C.

**[0313]** Aspect B17 is the filtration media of any one of Aspects B3 to B11, wherein the second layer of fine fibers comprises a layer of small fine fibers, then a layer of commingled small fine fibers and large fine fibers, and then a layer of large fine fibers.

**[0314]** Aspect B18 is the filtration media of any one of the preceding Aspects B1 to B17, wherein the fine fibers are compatible with at least one of a hydraulic fluid, fuel, or lubricant.

**[0315]** Aspect B19 is the filtration media of any one of the preceding Aspects B1 to B18, wherein the support layer comprises nylon.

**[0316]** Aspect B20 is the filtration media of any one of the preceding Aspects B1 to B19, wherein the support layer has an average mean flow pore size of at least 5 μm, at least 10 μm, at least 15 μm, at least 20 μm, or at least 25 μm and up to 10 μm, up to 15 μm, up to 20 μm, up to 25 μm, up to 30 μm, up to 35 μm, up to 40 μm, up to 50 μm, up to 60 μm, up to 70 μm, up to 80 μm, or up to 90 μm.

**[0317]** Aspect B21 is the filtration media of Aspect B20, wherein the average mean flow pore size is determined by capillary flow porometry.

**[0318]** Aspect B22 is the filtration media of any one of the preceding Aspects B1 to B21, wherein the support layer has an average maximum pore size of up to 10 μm, up to 15 μm, up to 20 μm, up to 25 μm, up to 30 μm, up to 35 μm, up to 40 μm, up to 50 μm, up to 60 μm, up to 70 μm, up to 80 μm, up to 90 μm, up to 100 μm, or up to 150 μm.

**[0319]** Aspect B23 is the filtration media of Aspect B22, wherein the average maximum pore size is determined by capillary flow porometry.

**[0320]** Aspect B24 is the filtration media of any one of the preceding Aspects B1 to B23, wherein the support layer has an average minimum pore size of at least 5 μm, at least 10 μm, at least 15 μm, at least 20 μm, at least 25 μm, at least 30 μm, at least 35 μm, at least 40 μm, or at least 50 μm.

**[0321]** Aspect B25 is the filtration media of Aspect B24, wherein the average minimum pore size is determined using capillary flow porometry.

**[0322]** Aspect B26 is the filtration media of any one of the preceding Aspects B1 to B25, wherein the support layer has

an average mean flow pore size, and wherein the average mean flow pore size of the support layer does not vary by more than 30%, does not vary by more than 25%, or does not vary by more than 15% across the length and width of the media.

**[0323]** Aspect B27 is the filtration media of any one of the preceding Aspects B1 to B26, wherein the filtration media comprises a composite comprising the support layer and the fine fiber layer; wherein the filtration media has a composite average maximum pore size of up to 14 μm, up to 15 μm, or up to 20 μm; or wherein the filtration media has a composite average maximum pore size of at least 0.1 μm; or both.

**[0324]** Aspect B28 is the filtration media of any one of the preceding Aspects B1 to B27, wherein the filtration media comprises a composite comprising the support layer and the fine fiber layer; wherein the filtration media has a composite average mean flow pore size of up to 11 μm, up to 9 μm, or up to 6 μm; or wherein the filtration media has a composite average mean flow pore size of at least 0.1 μm; or both.

**[0325]** Aspect B29 is the filtration media of Aspect B27 or B28, wherein the composite pore size is determined using capillary flow porometry.

**[0326]** Aspect B30 is the filtration media of any one of the preceding Aspects B1 to B29, wherein the first layer of fine fibers comprises fine fibers having a diameter at least 0.2 μm, at least 0.3 μm, or at least 0.4 μm greater than a fiber diameter of a fine fiber of the second fine fiber layer.

**[0327]** Aspect B31 is the filtration media of any one of the preceding Aspects B1 to B30, wherein the first fine fiber layer may have a thickness of at least 2 μm, at least 3 μm, at least 4 μm, or at least 5 μm; or wherein the first fine fiber layer may have a thickness of up to 5 μm, up to 10 μm, up to 30 μm, or up to 50 μm; or both.

**[0328]** Aspect B32 is the filtration media of any one of the preceding Aspects B1 to B31, wherein the second fine fiber layer may have a thickness of at least 2 μm, at least 3 μm, at least 4 μm, or at least 5 μm; or wherein the second fine fiber layer may have a thickness of up to 5 μm, up to 10 μm, up to 30 μm, up to 40 μm, or up to 45 μm; or both.

**[0329]** Aspect B33 is the filtration media of Aspect B31 or B32, wherein the thickness of the first fine fiber layer or the second fine fiber layer or both is determined using scanning electron microscopy (SEM).

**[0330]** Aspect B34 is the filtration media of any one of the preceding Aspects B1 to 33, wherein the support layer comprises a spunbond layer.

**[0331]** Aspect B35 is a filter element comprising the filtration media of any one of the preceding Aspects B1 to B34.

**[0332]** Aspect B36 is the filter element of Aspect B35, wherein the filter element comprises an efficiency layer, and the efficiency layer comprises the filtration media.

**[0333]** Aspect B37 is the filter element of Aspect B36, wherein the filter element further comprises a loading layer.

Exemplary Layered Filtration Media Aspects

**[0334]** Aspect C1 is a filtration media comprising: a support layer; a first layer of fine fibers and a second layer of fine fibers; wherein the first layer of fine fibers is deposited on the support layer; wherein the second layer of fine fibers is deposited on the first layer of fibers, and further wherein the second layer of fine fibers comprises small fine fibers and large fine fibers; wherein the large fine fibers have an average diameter at least 3 times the average diameter of the small fine fibers; wherein the small fine fibers are deposited on the first layer of fine fibers and the large fine fibers are deposited on the small fine fibers; and wherein the first layer of fine fibers comprises fine fibers having an average diameter at least 3 times the average fiber diameter of the small fine fibers of the second fine fiber layer.

**[0335]** Aspect C2 is the filtration media of Aspect C1, wherein the large fine fibers of the second layer of fine fibers comprise up to 10% of the fine fibers of the second layer of fine fibers.

**[0336]** Aspect C3 is the filtration media of Aspect C1 or C2, wherein the large fine fibers of the second layer of fine fibers comprise at least 5% and up to 7% of the fine fibers of the second layer of fine fibers.

**[0337]** Aspect C4 is the filtration media of Aspect C1, wherein the second layer of fine fibers comprises the layered fiber structure of one or more of Set A5, Set B, Set D5, Set E, Set 15, or Set J, of Table 1A-Table 1C.

**[0338]** Aspect C5 is the filtration media of any one of Aspects C2 to C4, wherein the proportion of the large fine fibers is determined based on spin time.

**[0339]** Aspect C6 is the filtration media of any one of Aspects C2 to C4, wherein the proportion of the large fine fibers is determined using microscopy or nano-CT.

**[0340]** Aspect C7 is the filtration media of any one of the preceding Aspects C1 to C6, wherein the large fine fibers of the second layer of fine fibers have an average diameter of at least 1 μm, or greater than 1 μm; or wherein the large fine fibers of the second layer of fine fibers have an average diameter of up to 1.1 μm, up to 1.2 μm, up to 1.3 μm, up to 1.4 μm, up to 1.5 μm, up to 2 μm, up to 3 μm, up to 4 μm, up to 5 μm, or up to 10 μm; or both.

**[0341]** Aspect C8 is the filtration media of any one of the preceding Aspects C1 to C7, wherein the first layer of fine fibers comprises fine fibers having an average diameter of at least 0.6 μm, at least 0.7 μm, at least 0.8 μm, or at least 0.9 μm, at least 1 μm, or greater than 1 μm; or wherein the first layer of fine fibers comprises fibers fine fibers have an average diameter of up to 1.1 μm, up to 1.2 μm, up to 1.3 μm, up to 1.4 μm, up to 1.5 μm, up to 2 μm, up to 3 μm, up to 4 μm, up to 5 μm, or up to 10 μm; or both.

**[0342]** Aspect C9 is the filtration media of any one of the preceding Aspects C1 to C8, wherein small fine fibers of the second layer of fine fibers have an average diameter of at least 0.2 μm; or wherein the small fine fibers of the second layer of fine fibers have an average diameter of up to 0.6 μm; or both.

**[0343]** Aspect C10 is the filtration media of any one of the preceding Aspects C1 to C9, wherein the support layer comprises nylon.

**[0344]** Aspect C11 is the filtration media of any one of the preceding Aspects C1 to C10, wherein the support layer has an average mean flow pore size of at least 5 μm, at least 10 μm, at least 15 μm, at least 20 μm, or at least 25 μm and up to 10 μm, up to 15 μm, up to 20 μm, up to 25 μm, up to 30 μm, up to 35 μm, up to 40 μm, up to 50 μm, up to 60 μm, up to 70 μm, up to 80 μm, or up to 90 μm.

**[0345]** Aspect C12 is the filtration media of Aspect C11, wherein the average minimum pore size is determined using capillary flow porometry.

**[0346]** Aspect C13 is the filtration media of any one of the preceding Aspects C1 to C12, wherein the support layer has an average maximum pore size of up to 10 μm, up to 15 μm, up to 20 μm, up to 25 μm, up to 30 μm, up to 35 μm, up to

40 μm, up to 50 μm, up to 60 μm, up to 70 μm, up to 80 μm, up to 90 μm, up to 100 μm, or up to 150 μm.

**[0347]** Aspect C14 is the filtration media of Aspect C13, wherein the average maximum pore size is determined using capillary flow porometry.

**[0348]** Aspect C15 is the filtration media of any one of the preceding Aspects C1 to C14, wherein the support layer has an average minimum pore size of at least 5 μm, at least 10 μm, at least 15 μm, at least 20 μm, at least 25 μm, at least 30 μm, at least 35 μm, at least 40 μm, or at least 50 μm.

**[0349]** Aspect C16 is the filtration media of Aspect C15, wherein the average minimum pore size is determined using capillary flow porometry.

**[0350]** Aspect C17 is the filtration media of any one of the preceding Aspects C1 to C16, wherein the support layer has an average mean flow pore size, and wherein the average mean flow pore size of the support layer does not vary by more than 30%, does not vary by more than 25%, or does not vary by more than 15% across the length and width of the media.

**[0351]** Aspect C18 is the filtration media of any one of the preceding Aspects C1 to C17, wherein the filtration media comprises a composite comprising the support layer and the fine fiber layer; wherein the filtration media has a composite average maximum pore size of up to 14 μm, up to 15 μm, or up to 20 μm; or wherein the filtration media has a composite average maximum pore size of at least 0.1 μm; or both.

**[0352]** Aspect C19 is the filtration media of any one of the preceding Aspects C1 to C18, wherein the filtration media comprises a composite comprising the support layer and the fine fiber layer; wherein the filtration media has a composite average mean flow pore size of up to 11 μm, up to 9 μm, or up to 6 μm; or wherein the filtration media has a composite average mean flow pore size of at least 0.1 μm; or both.

**[0353]** Aspect C20 is the filtration media of Aspect C18 or C19, wherein the composite pore size is determined using capillary flow porometry.

**[0354]** Aspect C21 is the filtration media of any one of the preceding Aspects C1 to C20, wherein the large fine fibers have a diameter at least 0.2 μm, at least 0.3 μm, or at least 0.4 μm greater than a diameter of the small fine fibers.

**[0355]** Aspect C22 is the filtration media of any one of the preceding Aspects C1 to C21, wherein the first fine fiber layer may have a thickness of at least 2 μm, at least 3 μm, at least 4 μm, or at least 5 μm; or wherein the first fine fiber layer may have a thickness of up to 5 μm, up to 10 μm, up to 30 μm, or up to 50 μm; or both.

**[0356]** Aspect C23 is the filtration media of any one of the preceding Aspects C1 to C22, wherein the second fine fiber layer may have a thickness of at least 2 μm, at least 3 μm, at least 4 μm, or at least 5 μm; or wherein the second fine fiber layer may have a thickness of up to 5 μm, up to 10 μm, up to 30 μm, up to 40 μm, or up to 45 μm; or both.

**[0357]** Aspect C24 is the filtration media of Aspect C22 or C23, wherein the thickness of the first fine fiber layer or the second fine fiber layer or both is determined using scanning electron microscopy (SEM).

**[0358]** Aspect C25 is the filtration media of any one of the preceding Aspects C1 to C24, wherein the support layer comprises a spunbond layer.

**[0359]** Aspect C26 is a filter element comprising the filtration media of any one of the preceding Aspects C1 to C25.

**[0360]** Aspect C27 is the filter element of Aspect C26, wherein the filter element comprises an efficiency layer, and the efficiency layer comprises the filtration media.

**[0361]** Aspect C28 is the filter element of Aspect C27, wherein the filter element further comprises a loading layer.

Exemplary Commingled Filtration Media Aspects

**[0362]** Aspect D1 is a filtration media comprising: a support layer; a first layer of fine fibers and a second layer of fine fibers; wherein the first layer of fine fibers is deposited on the support layer; wherein the second layer of fine fibers is deposited on the first layer of fibers, and further wherein the second layer of fine fibers comprises small fine fibers and large fine fibers; where the large fine fibers have an average diameter at least 3 times the average diameter of the small fine fibers; and wherein the small fine fibers are commingled with the large fine fibers; and wherein the first layer of fine fibers comprises fine fibers having an average diameter at least 3 times the average fiber diameter of the small fine fibers of the second fine fiber layer.

**[0363]** Aspect D2 is the filtration media of Aspect D1, wherein the large fine fibers of the second layer of fine fibers comprise up to 10% of the fine fibers of the second layer of fine fibers.

**[0364]** Aspect D3 is the filtration media of Aspect D1 or D2, wherein the large fine fibers of the second layer of fine fibers comprise at least 3% and up to 9%, at least 5% and up to 7%, or at least 4% and up to 8% of the fine fibers of the second layer of fine fibers.

**[0365]** Aspect D4 is the filtration media of Aspect D1, wherein the second layer of fine fibers comprises the commingled fiber structure of one or more of Set A6, Set D, Set D6, Set I, or Set L, of Table 1A-Table 1C.

**[0366]** Aspect D5 is the filtration media of any one of Aspects D2 to D4, wherein the proportion of the large fine fibers is determined based on spin time.

**[0367]** Aspect D6 is the filtration media of any one of Aspects D2 to D4, wherein the proportion of the large fine fibers is determined using microscopy or nano-CT.

**[0368]** Aspect D7 is the filtration media of any one of Aspects D1 to D6, wherein the large fine fibers of the second layer of fine fibers have an average diameter of at least 1 μm, or greater than 1 μm; or wherein the large fine fibers of the second layer of fine fibers have an average diameter of up to 1.1 μm, up to 1.2 μm, up to 1.3 μm, up to 1.4 μm, up to 1.5 μm, up to 2 μm, up to 3 μm, up to 4 μm, up to 5 μm, or up to 10 μm; or both.

**[0369]** Aspect D8 is the filtration media of any one of Aspects D1 to D7, wherein first layer of fine fibers comprises small fine fibers having an average diameter of at least 0.6 μm, at least 0.7 μm, at least 0.8 μm, or at least 0.9 μm, at least 1 μm, or greater than 1 μm; or wherein first layer of fine fibers comprises fine fibers having an average diameter of up to 1.1 μm, up to 1.2 μm, up to 1.3 μm, up to 1.4 μm, up to 1.5 μm, up to 2 μm, up to 3 μm, up to 4 μm, up to 5 μm, or up to 10 μm; or both.

**[0370]** Aspect D9 is the filtration media of any one of Aspects D1 to D8, wherein the small fine fibers of the second layer of fine fibers have an average diameter of at least 0.2 μm; or wherein the small fine fibers of the second layer of fine fibers have an average diameter of up to 0.3 μm, up to 0.4 μm, up to 0.5 μm, or up to 0.6 μm; or both.

**[0371]** Aspect D10 is the filtration media of any one of the preceding Aspects D1 to D9, wherein the support layer comprises nylon.

**[0372]** Aspect D11 is the filtration media of any one of the preceding Aspects D1 to D10, wherein the support layer has an average mean flow pore size of at least 5 μm, at least 10 μm, at least 15 μm, at least 20 μm, or at least 25 μm and up to 10 μm, up to 15 μm, up to 20 μm, up to 25 μm, up to 30 μm, up to 35 μm, up to 40 μm, up to 50 μm, up to 60 μm, up to 70 μm, up to 80 μm, or up to 90 μm.

**[0373]** Aspect D12 is the filtration media of Aspect D11, wherein the average mean flow pore size is determined using capillary flow porometry.

**[0374]** Aspect D13 is the filtration media of any one of the preceding Aspects D1 to D12, wherein the support layer has an average maximum pore size of up to 10 μm, up to 15 μm, up to 20 μm, up to 25 μm, up to 30 μm, up to 35 μm, up to 40 μm, up to 50 μm, up to 60 μm, up to 70 μm, up to 80 μm, up to 90 μm, up to 100 μm, or up to 150 μm.

**[0375]** Aspect D14 is the filtration media of Aspect D13, wherein the average maximum pore size is determined using capillary flow porometry.

**[0376]** Aspect D15 is the filtration media of any one of the preceding Aspects D1 to D14, wherein the support layer has an average minimum pore size of at least 5 μm, at least 10 μm, at least 15 μm, at least 20 μm, at least 25 μm, at least 30 μm, at least 35 μm, at least 40 μm, or at least 50 μm.

**[0377]** Aspect D16 is the filtration media of Aspect D15, wherein the average minimum pore size is determined using capillary flow porometry.

**[0378]** Aspect D17 is the filtration media of any one of the preceding Aspects D1 to D16, wherein the support layer has an average mean flow pore size, and wherein the average mean flow pore size of the support layer does not vary by more than 30%, does not vary by more than 25%, or does not vary by more than 15% across the length and width of the media.

**[0379]** Aspect D18 is the filtration media of any one of the preceding Aspects D1 to D17, wherein the filtration media comprises a composite comprising the support layer and the fine fiber layer; wherein the filtration media has a composite average maximum pore size of up to 14 μm, up to 15 μm, or up to 20 μm; or wherein the filtration media has a composite average maximum pore size of at least 0.1 μm; or both.

**[0380]** Aspect D19 is the filtration media of any one of the preceding Aspects D1 to D18, wherein the filtration media comprises a composite comprising the support layer and the fine fiber layer; wherein the filtration media has a composite average mean flow pore size of up to 11 μm, up to 9 μm, or up to 6 μm; or wherein the filtration media has a composite average mean flow pore size of at least 0.1 μm; or both.

**[0381]** Aspect D20 is the filtration media of Aspect D18 or D19, wherein the composite pore size is determined using capillary flow porometry.

**[0382]** Aspect D21 is the filtration media of any one of the preceding Aspects D1 to D20, wherein the second layer of fine fibers comprises small fine fibers and large fine fibers, the large fine fibers having a diameter at least 0.2 μm, at least 0.3 μm, or at least 0.4 μm greater than a diameter of the small fine fibers.

**[0383]** Aspect D22 is the filtration media of any one of the preceding Aspects D1 to D21, wherein the first layer of fine fibers comprises fine fibers having a diameter at least 0.2 μm, at least 0.3 μm, or at least 0.4 μm greater than a fiber diameter of a fine fiber of the second fine fiber layer.

**[0384]** Aspect D23 is the filtration media of any one of the preceding Aspects D1 to D22, wherein the first fine fiber layer has a thickness of at least 2 μm, at least 3 μm, at least 4 μm, or at least 5 μm; or wherein the first fine fiber layer has a thickness of up to 5 μm, up to 10 μm, up to 30 μm, or up to 50 μm; or both.

**[0385]** Aspect D24 is the filtration media of any one of the preceding Aspects D1 to D23, wherein the second fine fiber layer has a thickness of at least 2 μm, at least 3 μm, at least 4 μm, or at least 5 μm; or wherein the second fine fiber layer has a thickness of up to 5 μm, up to 10 μm, up to 30 μm, up to 40 μm, or up to 45 μm; or both.

**[0386]** Aspect D25 is the filtration media of Aspect D23 or D24, wherein the thickness of the first fine fiber layer or the second fine fiber layer or both is determined using scanning electron microscopy (SEM).

**[0387]** Aspect D26 is the filtration media of any one of the preceding Aspects D1 to D25, wherein the support layer comprises a spunbond layer.

**[0388]** Aspect D27 is a filter element comprising the filtration media of any one of the preceding Aspects D1 to D26.

**[0389]** Aspect D28 is the filter element of Aspect D27, wherein the filter element comprises an efficiency layer, and the efficiency layer comprises the filtration media.

**[0390]** Aspect D29 is the filter element of Aspect D28, wherein the filter element further comprises a loading layer.

Exemplary Product by Process Aspects Including at Least One Fine Fiber Layer

**[0391]** Aspect E1 is a filtration media comprising a support layer and a first layer of fine fibers; wherein the first layer of fine fibers is deposited on the support layer and comprises large fine fibers and small fine fibers, the large fine fibers having an average diameter of at least 3 times the average diameter of the small fine fibers, and wherein at least some of the fine fibers are prepared by a method comprising: providing a fiber-forming polymer; providing a polymer-reactive resinous aldehyde composition, wherein the polymer-reactive resinous aldehyde composition is reactive with the fiber-forming polymer; and combining the fiber-forming polymer and reactive resinous aldehyde composition to form a plurality of fine fibers.

**[0392]** Aspect E2 is filtration media comprising a support layer and a first layer of fine fibers; wherein the first layer of fine fibers is deposited on the support layer and comprises large fine fibers and small fine fibers, the large fine fibers having an average diameter of at least 3 times the average diameter of the small fine fibers, and wherein at least some of the fine fibers are prepared by a method comprising: providing a fiber-forming polymer, wherein the fiber-forming polymer comprises a nonreactive polymer, that is a polymer unable to crosslink with the polymer-non-reactive resinous aldehyde composition; providing a polymer-non-reactive resinous aldehyde composition, wherein the polymer-non-reactive resinous aldehyde composition comprises one or more reactive groups that are capable of self-crosslinking; and combining the fiber-forming polymer and reactive resinous aldehyde composition to form a plurality of fine fibers.

**[0393]** Aspect E3 is a filtration media comprising a support layer and a first layer of fine fibers; wherein the first

layer of fine fibers is deposited on the support layer and comprises large fine fibers and small fine fibers, the large fine fibers having an average diameter of at least 3 times the average diameter of the small fine fibers, and wherein at least some of the fine fibers are prepared by a method comprising: providing at least one fiber-forming polymer; providing at least two reactive additives reactive with each other, and optionally reactive with the fiber-forming polymer; and combining the at least one fiber-forming polymer and the at least two reactive additives under conditions effective to form a plurality of fine fibers.

**[0394]** Aspect E4 is the filtration media of any one of the preceding Aspects E1 to E3, wherein the large fine fibers of the first layer of fine fibers have an average diameter of at least 1 μm, or greater than 1 μm; or wherein the large fine fibers of the first layer of fine fibers have an average diameter of up to 1.1 μm, up to 1.2 μm, up to 1.3 μm, up to 1.4 μm, up to 1.5 μm, up to 2 μm, up to 3 μm, up to 4 μm, up to 5 μm, or up to 10 μm. or both.

**[0395]** Aspect E5 is the filtration media of any one of the preceding Aspects E1 to E4, wherein the first layer of fine fibers comprises small fine fibers, wherein small fine fibers have an average diameter of at least 0.2 μm; or wherein the small fine fibers have an average diameter of up to 0.3 μm, up to 0.4 μm, up to 0.5 μm, or up to 0.6 μm; or both.

**[0396]** Aspect E6 is the filtration media of any one of the preceding Aspects E1 to E5, wherein the first layer of fine fibers comprises up to 10% large fine fibers or up to 20% large fine fibers.

**[0397]** Aspect E7 is the filtration media of any one of the preceding Aspects E1 to E6, wherein the first layer of fine fibers comprises at least 3% and up to 9% large fine fibers, at least 5% and up to 7% large fine fibers, or at least 4% and up to 8% large fine fibers.

**[0398]** Aspect E8 is the filtration media of any one of the preceding Aspects E1 to E7, wherein the first layer of fine fibers comprises the proportion of large fine fibers of one or more of Set A5, Set A6, Set B, Set D, Set D5, Set D6, Set E, Set I, Set I5, Set I6, Set J, or Set L of Table 1A-Table 1C.

**[0399]** Aspect E9 is the filtration media of any one of Aspects E6 to E8, wherein the proportion of the large fine fibers is determined based on spin time.

**[0400]** Aspect 10 is the filtration media of any one of Aspects E6 to E8, wherein the proportion of the large fine fibers is determined using microscopy or nano-CT.

**[0401]** Aspect E11 is the filtration media of any one of Aspects 1 to 10, wherein the first layer of fine fibers comprises a layered fiber structure.

**[0402]** Aspect E12 is the filtration media of Aspect E11, wherein the first layer of fine fibers comprises the layered fiber structure of one or more of Set A5, Set B, Set D5, Set E, Set 15, or Set J, of Table 1A-Table 1C.

**[0403]** Aspect E13 is the filtration media of Aspect E11, wherein the first layer of fine fibers comprises small fine fibers and large fine fibers, and wherein within the first layer of fine fibers, the small fine fibers are deposited on a first sub-layer of fine fibers and a second sub-layer of large fine fibers are deposited on the small fine fibers.

**[0404]** Aspect E14 is the filtration media of any one of Aspects E1 to E10, wherein the first layer of fine fibers comprises a commingled fiber structure.

**[0405]** Aspect E15 is the filtration media of Aspect E14, wherein the first layer of fine fibers comprises the commingled fiber structure of one or more of Set A6, Set D, Set D6, Set I, or Set L, of Table 1A-Table 1C.

**[0406]** Aspect E16 is the filtration media of any one of the preceding Aspects E1 to E15, wherein the fine fibers are compatible with at least one of a hydraulic fluid, fuel, or lubricant.

**[0407]** Aspect E17 is the filtration media of any one of the preceding Aspects E1 to E16, wherein the support layer comprises nylon.

**[0408]** Aspect E18 is the filtration media of any one of the preceding Aspects E1 to E17, wherein the support layer has an average mean flow pore size of at least 5 μm, at least 10 μm, at least 15 μm, at least 20 μm, or at least 25 μm and up to 10 μm, up to 15 μm, up to 20 μm, up to 25 μm, up to 30 μm, up to 35 μm, up to 40 μm, up to 50 μm, up to 60 μm, up to 70 μm, up to 80 μm, or up to 90 μm.

**[0409]** Aspect E19 is the filtration media of Aspect E18, wherein the average mean flow pore size is determined using capillary flow porometry.

**[0410]** Aspect E20 is the filtration media of any one of the preceding Aspects E1 to E19, wherein the support layer has an average maximum pore size of up to 10 μm, up to 15 μm, up to 20 μm, up to 25 μm, up to 30 μm, up to 35 μm, up to 40 μm, up to 50 μm, up to 60 μm, up to 70 μm, up to 80 μm, up to 90 μm, up to 100 μm, or up to 150 μm.

**[0411]** Aspect E21 is the filtration media of Aspect E20, wherein the average maximum pore size is determined using capillary flow porometry.

**[0412]** Aspect E22 is the filtration media of any one of the preceding Aspects E1 to E21, wherein the support layer has an average minimum pore size of at least 5 μm, at least 10 μm, at least 15 μm, at least 20 μm, at least 25 μm, at least 30 μm, at least 35 μm, at least 40 μm, or at least 50 μm.

**[0413]** Aspect E23 is the filtration media of Aspect E22, wherein the average minimum pore size is determined using capillary flow porometry.

**[0414]** Aspect E24 is the filtration media of any one of the preceding Aspects E1 to E23, wherein the support layer has an average mean flow pore size, and wherein the average mean flow pore size of the support layer does not vary by more than 30%, does not vary by more than 25%, or does not vary by more than 15% across the length and width of the media.

**[0415]** Aspect E25 is the filtration media of any one of the preceding Aspects E1 to E24, wherein the filtration media comprises a composite comprising the support layer and the fine fiber layer; wherein the filtration media has a composite average maximum pore size of up to 14 μm, up to 15 μm, or up to 20 μm; or wherein the filtration media has a composite average maximum pore size of at least 0.1 μm; or both.

**[0416]** Aspect E26 is the filtration media of any one of the preceding Aspects E1 to E25, wherein the filtration media comprises a composite comprising the support layer and the fine fiber layer; wherein the filtration media has a composite average mean flow pore size of up to 11 μm, up to 9 μm, or up to 6 μm; or wherein the filtration media has a composite average mean flow pore size of at least 0.1 μm; or both.

**[0417]** Aspect E27 is the filtration media of Aspect E25 or E26, wherein the composite pore size is determined using capillary flow porometry.

**[0418]** Aspect E28 is the filtration media of any one of the preceding Aspects E1 to E27, wherein the large fine fibers have a diameter at least 0.2 μm, at least 0.3 μm, or at least 0.4 μm greater than a diameter of the small fine fibers.

**[0419]** Aspect E29 is the filtration media of any one of the preceding Aspects E1 to E28, wherein the first fine fiber layer has a thickness of at least 2 μm, at least 3 μm, at least 4 μm, or at least 5 μm; or wherein the first fine fiber layer has a thickness of up to 5 μm, up to 10 μm, up to 30 μm, or up to 50 μm; or both.

**[0420]** Aspect E30 is the filtration media of Aspect E29, wherein the thickness of the first fine fiber layer is determined using scanning electron microscopy (SEM).

**[0421]** Aspect E31 is the filtration media of any one of the preceding Aspects E1 to E30, wherein the support layer comprises a spunbond layer.

**[0422]** Aspect E32 is the filtration media of any one of the preceding Aspects E1 to E31, wherein the filtration media further comprises a second fine fiber layer.

**[0423]** Aspect E33 is a filter element comprising the filtration media of any one of the preceding Aspects E1 to E32.

**[0424]** Aspect E34 is the filter element of Aspect E33, wherein the filter element comprises an efficiency layer, and the efficiency layer comprises the filtration media.

**[0425]** Aspect E35 is the filter element of Aspect E34, wherein the filter element further comprises a loading layer.

Exemplary Product by Process Aspects Including at Least Two Fine Fiber Layers

**[0426]** Aspect F1 is a filtration media comprising a support layer, a first layer of fine fibers, and a second layer of fine fibers; wherein the first layer of fine fibers is deposited on the support layer and comprises fibers having an average diameter at least 3 times the average fiber diameter of a fine fiber of the second fine fiber layer; wherein the second layer of fine fibers is deposited on the first layer of fibers; and wherein at least some of the fine fibers are prepared by a method comprising: providing a fiber-forming polymer; providing a polymer-reactive resinous aldehyde composition, wherein the polymer-reactive resinous aldehyde composition is reactive with the fiber-forming polymer; and combining the fiber-forming polymer and reactive resinous aldehyde composition to form a plurality of fine fibers.

**[0427]** Aspect F2 is a filtration media comprising a support layer; a first layer of fine fibers and a second layer of fine fibers; wherein the first layer of fine fibers is deposited on the support layer and comprises fibers having an average diameter at least 3 times the average fiber diameter of a fine fiber of the second fine fiber layer; wherein the second layer of fine fibers is deposited on the first layer of fibers; and wherein at least some of the fine fibers are prepared by a method comprising: providing a fiber-forming polymer, wherein the fiber-forming polymer comprises a nonreactive polymer, that is a polymer unable to crosslink with the polymer-non-reactive resinous aldehyde composition; providing a polymer-non-reactive resinous aldehyde composition, wherein the polymer-non-reactive resinous aldehyde composition comprises one or more reactive groups that are capable of self-crosslinking; and combining the fiber-forming polymer and reactive resinous aldehyde composition to form a plurality of fine fibers.

**[0428]** Aspect F3 is a filtration media comprising a support layer, a first layer of fine fibers, and a second layer of fine fibers; wherein the first layer of fine fibers is deposited on the support layer and comprises fibers having an average diameter at least 3 times the average fiber diameter of a fine fiber of the second fine fiber layer; wherein the second layer of fine fibers is deposited on the first layer of fibers; and wherein at least some of the fine fibers are prepared by a method comprising: providing at least one fiber-forming polymer; providing at least two reactive additives reactive with each other, and optionally reactive with the fiber-forming polymer; and combining the at least one fiber-forming polymer and the at least two reactive additives under conditions effective to form a plurality of fine fibers.

**[0429]** Aspect F4 is the filtration media of any one of the preceding Aspects F1 to F3, wherein the fine fibers of the first layer of fine fibers have an average diameter of greater than 0.6 μm, at least 0.7 μm, at least 0.8 μm, at least 0.8 μm, at least 1 μm, or greater than 1 μm; or wherein the fine fibers of the first layer of fine fibers have an average diameter of up to 1.1 μm, up to 1.2 μm, up to 1.3 μm, up to 1.4 μm, up to 1.5 μm, up to 2 μm, up to 3 μm, up to 4 μm, up to 5 μm, or up to 10 μm; or both.

**[0430]** Aspect F5 is the filtration media of any one of the preceding Aspects F1 to F4, wherein the second layer of fine fibers comprises fine fibers of mixed diameters.

**[0431]** Aspect F6 is the filtration media of Aspect F5, wherein the second layer of fine fibers comprises large fine fibers having an average diameter of 3 times greater than the average diameter of small fine fibers.

**[0432]** Aspect F7 is the filtration media of Aspect F5 or F6, wherein the second layer of fine fibers comprises large fine fibers and small fine fibers, wherein the large fine fibers have an average diameter of at least 1 μm, or greater than 1 μm; or wherein the large fine fiber have an average diameter of to 1.1 μm, up to 1.2 μm, up to 1.3 μm, up to 1.4 μm, up to 1.5 μm, up to 2 μm, up to 3 μm, up to 4 μm, up to 5 μm, or up to 10 μm; or both; and wherein the small fine fibers have an average diameter of at least 0.2 μm; or wherein the small fine fibers have an average diameter of up to 0.6 μm; or both.

**[0433]** Aspect F8 is the filtration media of Aspect F5 or F6, wherein the large fine fibers have an average diameter of greater than 1 μm.

**[0434]** Aspect F9 is the filtration media of any one of Aspects F5 to F8, wherein the second layer of fine fibers comprises up to 10% large fine fibers or up to 20% large fine fibers. Aspect F10 is the filtration media of any one of Aspects F5 to F8, wherein the second layer of fine fibers comprises at least 3% and up to 9% large fine fibers, at least 5% and up to 7% large fine fibers, or at least 4% and up to 8% large fine fibers.

**[0435]** Aspect F11 is the filtration media of any one of Aspects F5 to F8, wherein the second layer of fine fibers comprises the proportion of large fine fibers of one or more of Set A5, Set A6, Set B, Set D, Set D5, Set D6, Set E, Set I, Set I5, Set I6, Set J, or Set L of Table 1A-Table 1C.

**[0436]** Aspect F12 is the filtration media of any one of Aspects F9 to F11, wherein the proportion of the large fine fibers is determined based on spin time.

**[0437]** Aspect F13 is the filtration media of any one of Aspects F9 to F11, wherein the proportion of the large fine fibers is determined using microscopy or nano-CT.

**[0438]** Aspect F14 is the filtration media of any one of Aspects F5 to F13, wherein the second layer of fine fibers comprises a layered fiber structure.

**[0439]** Aspect F15 is the filtration media of Aspect F14, wherein the second layer of fine fibers comprises the layered fiber structure of one or more of Set A5, Set B, Set D5, Set E, Set 15, or Set J, of Table 1A-Table 1C.

**[0440]** Aspect F16 is the filtration media of Aspect F14, wherein the second layer of fine fibers comprises small fine fibers and large fine fibers, and wherein the small fine fibers are deposited on the first layer of fine fibers, and wherein the large fine fibers are deposited on the small fine fibers.

**[0441]** Aspect F17 is the filtration media of any one of Aspects F5 to F13, wherein the second layer of fine fibers comprises a commingled fiber structure.

**[0442]** Aspect F18 is the filtration media of Aspect F17, wherein the second layer of fine fibers comprises the commingled fiber structure of one or more of Set A6, Set D, Set D6, Set I, or Set L, of Table 1A-Table 1C.

**[0443]** Aspect F19 is the filtration media of any one of Aspects F5 to F13, wherein the second layer of fine fibers comprises small fine fibers and large fine fibers, and wherein within the second layer of fine fibers, the small fine fibers are deposited on a first sub-layer of large fine fibers and a second sub-layer of large fine fibers are deposited on the small fine fibers.

**[0444]** Aspect F20 is the filtration media of any one of the preceding Aspects F1 to F19, wherein the fine fibers are compatible with at least one of a hydraulic fluid, fuel, or lubricant.

**[0445]** Aspect F21 is the filtration media of any one of the preceding Aspects F1 to F20, wherein the support layer comprises nylon.

**[0446]** Aspect F22 is the filtration media of any one of the preceding Aspects F1 to F21, wherein the support layer has an average mean flow pore size of at least 5 μm, at least 10 μm, at least 15 μm, at least 20 μm, or at least 25 μm and up to 10 μm, up to 15 μm, up to 20 μm, up to 25 μm, up to 30 μm, up to 35 μm, up to 40 μm, up to 50 μm, up to 60 μm, up to 70 μm, up to 80 μm, or up to 90 μm.

**[0447]** Aspect F23 is the filtration media of Aspect F22, wherein the average maximum pore size is determined using capillary flow porometry.

**[0448]** Aspect F24 is the filtration media of any one of the preceding Aspects F1 to F23, wherein the support layer has an average maximum pore size of up to 10 μm, up to 15 μm, up to 20 μm, up to 25 μm, up to 30 μm, up to 35 μm, up to 40 μm, up to 50 μm, up to 60 μm, up to 70 μm, up to 80 μm, up to 90 μm, up to 100 μm, or up to 150 μm.

**[0449]** Aspect F25 is the filtration media of Aspect F24, wherein the average maximum pore size is determined using capillary flow porometry.

**[0450]** Aspect F26 is the filtration media of any one of the preceding Aspects F1 to F25, wherein the support layer has an average minimum pore size of at least 5 μm, at least 10 μm, at least 15 μm, at least 20 μm, at least 25 μm, at least 30 μm, at least 35 μm, at least 40 μm, or at least 50 μm.

**[0451]** Aspect F27 is the filtration media of Aspect F25, wherein the average minimum pore size is determined using capillary flow porometry.

**[0452]** Aspect F28 is the filtration media of any one of the preceding Aspects F1 to F27, wherein the support layer has an average mean flow pore size, and wherein the average mean flow pore size of the support layer does not vary by more than 30%, does not vary by more than 25%, or does not vary by more than 15% across the length and width of the media.

**[0453]** Aspect F29 is the filtration media of any one of the preceding Aspects F1 to F28, wherein the filtration media comprises a composite comprising the support layer and the fine fiber layer; wherein the filtration media has a composite average maximum pore size of up to 14 μm, up to 15 μm, or up to 20 μm; or wherein the filtration media has a composite average maximum pore size of at least 0.1 μm; or both.

**[0454]** Aspect F30 is the filtration media of any one of the preceding Aspects F1 to F29, wherein the filtration media comprises a composite comprising the support layer and the fine fiber layer; wherein the filtration media has a composite average mean flow pore size of up to 11 μm, up to 9 μm, or up to 6 μm; or wherein the filtration media has a composite average mean flow pore size of at least 0.1 μm; or both.

**[0455]** Aspect F31 is the filtration media of Aspect F29 or F30, wherein the composite pore size is determined using capillary flow porometry.

**[0456]** Aspect F32 is the filtration media of any one of the preceding Aspects F1 to F31, wherein the first layer of fine fibers comprises fine fibers having a diameter at least 0.2 μm, at least 0.3 μm, or at least 0.4 μm greater than a fiber diameter of a fine fiber of the second fine fiber layer.

**[0457]** Aspect F33 is the filtration media of any one of the preceding Aspects F1 to F32, wherein the first fine fiber layer has a thickness of at least 2 μm, at least 3 μm, at least 4 μm, or at least 5 μm; or wherein the first fine fiber layer has a thickness of up to 5 μm, up to 10 μm, up to 30 μm, or up to 50 μm; or both.

**[0458]** Aspect F34 is the filtration media of any one of the preceding Aspects F1 to F33, wherein the second fine fiber layer has a thickness of at least 2 μm, at least 3 μm, at least 4 μm, or at least 5 μm; or wherein the second fine fiber layer has a thickness of up to 5 μm, up to 10 μm, up to 30 μm, up to 40 μm, or up to 45 μm; or both.

**[0459]** Aspect F35 is the filtration media of Aspect F33 or F34, wherein the thickness of the first fine fiber layer or the second fine fiber layer or both is determined using scanning electron microscopy (SEM).

**[0460]** Aspect F36 is the filtration media of any one of the preceding Aspects F1 to F35, wherein the support layer comprises a spunbond layer.

**[0461]** Aspect F37 is a filter element comprising the filtration media of any one of the preceding Aspects F1 to F36.

**[0462]** Aspect F38 is the filter element of Aspect F37, wherein the filter element comprises an efficiency layer, and the efficiency layer comprises the filtration media.

**[0463]** Aspect F39 is the filter element of Aspect F38, wherein the filter element further comprises a loading layer.

**[0464]** The present invention is illustrated by the following examples. It is to be understood that the particular examples, materials, amounts, and procedures are to be interpreted broadly in accordance with the scope and spirit of the invention as set forth herein.

## EXAMPLES

### Preparation of Polymer Solutions

**[0465]** To prepare Solution 1, a nylon copolymer resin (SVP 651 obtained from Shakespeare Co., Columbia, S.C., a terpolymer having a number average molecular weight of 21,500-24,800 comprising 45% nylon-6, 20% nylon-6,6 and 25% nylon-6,10) was dissolved in alcohol (ethanol, 190 proof) and heated to 60° C. to produce a 9% nylon solids solution. After cooling, a melamine-formaldehyde resin (CYMEL 1133, Cytec Industries of West Paterson, N.J.) was added to the solution to achieve a weight ratio of melamine-formaldehyde resin to nylon of 20:100 parts by weight. The

melamine-formaldehyde resin acts as a crosslinking agent. Additionally, para-toluene sulfonic acid (7%, based on polymer solids) was added to the solution. The solution was agitated until uniform. Solution 1 was used to prepare 0.25 μm fibers.

**[0466]** Solution 2 was prepared as described for Solution 1 (and also resulted in a weight ratio of melamine-formaldehyde resin to nylon of 20:100 parts by weight) except a 17% nylon solids solution was used. Solution 2 was used to prepare 1 μm fibers.

**[0467]** Viscosity values of 30±5 cP and 300±5 cP for Solution 1 and 2, respectively, were measured at 25° C. with a Brookfield LV DV-I Prime Viscometer in conjunction with a Fisher Scientific Model 8005 temperature-controlled water bath.

**[0468]** Solution 3 was prepared as described for Solution 1 (and also resulted in a weight ratio of melamine-formaldehyde resin to nylon of 20:100 parts by weight) except a 12% nylon solids solution was used and no melamine-formaldehyde resin was added. Solution 3 had a viscosity of 77±5 cP measured at 25° C. with a Brookfield LV DV-I Prime Viscometer in conjunction with a Fisher Scientific Model 8005 temperature-controlled water bath. Solution 3 was used to prepare 0.5 μm fibers.

**[0469]** To prepare Solution 4, a copolyamide (Griltex D 1523A, EMS-Griltech, Switzerland) was dissolved in a solvent mixture of ethanol, benzyl alcohol, and water (ethanol:benzyl alcohol:water 16:1:1 by weight) and heated to 60° C. to produce a 21% (w/w) solution. Solution 4 had a viscosity of 473±10 cP measured at 25° C. with a Brookfield LV DV-I Prime Viscometer in conjunction with a Fisher Scientific Model 8005 temperature-controlled water bath. Solution 4 was used to prepare 1.4 μm fibers.

Preparation of Samples by Pendant Drop

**[0470]** Samples were prepared using a pendant drop apparatus, that is, a syringe filled with polymer solution. A high voltage is applied to a needle attached to the syringe and the polymer solution is pumped at a specified pump rate. As the drop of the polymer solution emerges from the needle, it forms a Taylor cone under the influence of the electrostatic field. At sufficiently high voltages, a jet is emitted from the Taylor cone which undergoes extension and fine fibers are formed and deposited on the media attached to a rotating mandrel which acts as the collector.

**[0471]** Fibers were formed onto a support layer wrapped around a cylinder (having a diameter 4 inches and rotating at 300 rpm) by electrospinning at a voltage of 24 kV and at a distance of 4 inches from the syringe or syringes delivering the polymer solution or solutions at a pump rate of 0.075 mL/min. After electrospinning, the formed fine fibers were thermally treated at 140° C. for 10 minutes.

Method 1:

**[0472]** A mixed fiber layer was deposited on a 0.2 mm thick, spunbond nylon scrim having a basis weight of 70 g/m$^2$ and a solidity of 28% (Media Grade 23200, Cerex Advanced Fibers, Cantonment, Fla.) by co-spinning two different electrospinning precursor solutions (Solution 1 and Solution 2) from two different syringes, delivered at the same pump rate (0.075 mL/minute) and for the same duration (5 minutes). Two control samples were separately prepared using the same pump rate and duration, by spinning Solution 1 or Solution 2 from a single syringe to produce a layer including only small fine fibers or large fine fibers, respectively.

**[0473]** All samples were subjected to a post-synthesis treatment to improve robustness via cross-linking. After electrospinning, formed fibers were thermally treated at 140° C. for 10 minutes.

Method 2:

**[0474]** A series of mixed fiber layers were deposited on a 0.2 mm thick, spunbond nylon scrim having a basis weight of 70 g/m$^2$ and a solidity of 28% (Media Grade 23200, Cerex Advanced Fibers, Cantonment, Fla.) by co-spinning Solution 1 and Solution 2 from two different syringes, delivered at the same pump rate (0.075 mL/minute) and for the same duration. Two control samples were separately prepared using the same pump rate and duration, by co-spinning either Solution 1 or Solution 2 from two syringes to produce a layer including only small fine fibers or large fine fibers, respectively. In contrast to Method 1, co-spinning either Solution 1 or Solution 2 from two syringes (instead of one syringe) resulted in more similar basis weights between the control samples and the samples including mixed fiber layers.

**[0475]** All samples were subjected to a post-synthesis treatment to improve robustness via cross-linking. After electrospinning, formed fibers were thermally treated at 140° C. for 10 minutes.

Method 3:

**[0476]** A series of fiber layers having fibers of different diameters were deposited on a 0.2 mm thick, spunbond nylon scrim having a basis weight of 70 g/m$^2$ and a solidity of 28% (Media Grade 23200, Cerex Advanced Fibers, Cantonment, Fla.) by alternatingly ("pulsed") spinning from one of two syringes containing Solution 1 or Solution 2, delivered at the same pump rate (0.075 mL/min) and alternatingly according to the timing sequences in Table 1A.

**[0477]** All samples were subjected to a post-synthesis treatment to improve robustness via cross-linking. After electrospinning, formed fibers were thermally treated at 140° C. for 10 minutes.

Method 4:

**[0478]** A series of mixed fiber structures were deposited on a 0.2 mm thick, spunbond nylon scrim having a basis weight of 70 g/m$^2$ and a solidity of 28% (Media Grade 23200, Cerex Advanced Fibers, Cantonment, Fla.) using a two-step procedure.

**[0479]** In the first step, large fine fibers (equivalent to 0.43 g/m$^2$ coverage) were deposited onto the scrim to act as an underlying support layer for subsequent fibers by delivering Solution 2 at a pump rate of (0.075 mL/min) for 2 minutes.

**[0480]** In the second step, a layer of fine fibers of mixed diameters was deposited by alternatingly ("pulsed") spinning from either one of two syringes containing Solution 1 or Solution 2 (for small fine fibers and large fine fibers, respectively) delivered at the same pump rate (0.075 mL/min) and alternatingly according to the timing sequences in Table 1A.

**[0481]** All samples, with approximate total basis weight ranging from 0.65 to 0.86 g/m$^2$, were subjected to a post-

synthesis treatment to improve robustness via cross-linking. After electrospinning, formed fibers were thermally treated at 140° C. for 10 minutes.

Method 5

**[0482]** A series of structures having varied basis weight contributions from the small fine fiber component were deposited on a 0.2 mm thick, spunbond nylon scrim having a basis weight of 70 g/m$^2$ and a solidity of 28% (Media Grade 23200, Cerex Advanced Fibers, Cantonment, Fla.) using a two-step procedure.

**[0483]** In the first step, large fine fibers (equivalent to 0.43 g/m$^2$ coverage) were deposited onto the scrim to act as an underlying support layer for subsequent fibers by delivering Solution 2 at a pump rate of (0.075 mL/min) for 2 minutes.

**[0484]** In the second step, a layer of small fine fibers was deposited by delivering Solution 1 at a pump rate of 0.075 mL/min. The basis weight of the small fine fiber layer was 0.09 g/m$^2$, 0.10 g/m$^2$, 0.22 g/m$^2$, 0.31 g/m$^2$, 0.45 g/m$^2$, or 0.56 g/m$^2$, and was achieved by using an electrospinning duration of to 48 seconds, 60 seconds, 120 seconds, 168 seconds, 240 seconds, or 300 seconds, respectively. After electrospinning, formed fibers were thermally treated at 140° C. for 10 minutes.

of small fine fibers, then a layer of commingled small fine fibers and large fine fibers, and topped by a layer of large fine fibers (Large/Small/Commingled/Large, or L/S/Commingled/L).

**[0486]** Large fine fibers (equivalent to 0.43 g/m$^2$ coverage) were deposited onto the scrim by spinning Solution 2 for 2 minutes. Without wishing to be bound by theory, it is believed the large fine fibers act as an underlying support layer for subsequent fiber layers. Next, a second layer of small fine fibers (equivalent to 0.22 g/m$^2$ coverage) was deposited by spinning Solution 1 for 2 minutes. If included, an intermediate (commingled) layer including both small fine fibers and large fine fibers was added by alternatingly ("pulsed") spinning from a syringe containing Solution 1 or Solution 2, for small fine fibers and large fine fibers, respectively, according to the timing sequences in Table 1A. Finally, a top layer of large fine fibers (equivalent to 0.43 g/m$^2$ coverage) was deposited by spinning Solution 2 for 2 minutes. All solutions were delivered at a pump rate of 0.075 mL/min.

**[0487]** All samples, with approximate total basis weight ranging from 1.31 to 1.52 g/m$^2$, were subjected to a post-synthesis treatment to improve robustness via cross-linking. After electrospinning, formed fibers were thermally treated at 140° C. for 10 minutes.

TABLE 1A

Pulsed electrospinning sequence

| Sample ID | Pulsed spinning sequence (2 minutes total duration) | Structure and composition* | Basis weight (g/m$^2$) (excluding large fine fiber support layer) | Basis weight (g/m$^2$) (all fine fibers) | % Solidity ** |
|---|---|---|---|---|---|
| Set A | 2 min Solution 1 only | 100% small fine fibers | 0.22 | 0.65 | 27 |
| Set A5 | 102 sec Solution 1 + 18 sec Solution 2 | Layered, 2% large fine fibers | 0.25 | 0.68 | 30 |
| Set A6 | (51 sec Solution 1 + 9 sec Solution 2) ×2 | Commingled, 2% large fine fibers | 0.25 | 0.68 | 31 |
| Set B | 90 sec Solution 1 + 30 sec Solution 2 | Layered, 5% large fine fibers | 0.28 | 0.71 | 33 |
| Set D | (30 sec Solution 1 + 10 sec Solution 2) ×3 | Commingled, 5% large fine fibers | 0.28 | 0.71 | 30 |
| Set D5 | 72 sec Solution 1 + 48 sec Solution 2 | Layered, 7% large fine fibers | 0.31 | 0.74 | 32 |
| Set D6 | (18 sec Solution 1 + 12 sec Solution 2) ×4 | Commingled, 7% large fine fibers | 0.31 | 0.74 | 30 |
| Set E | 1 min Solution 1 + 1 min Solution 2 | Layered, 10% large fine fibers | 0.33 | 0.76 | 33 |
| Set I | (10 sec Solution 1 + 10 sec Solution 2) ×6 | Commingled, 10% large fine fibers | 0.33 | 0.76 | 34 |
| Set I5 | 42 sec Solution 1 + 78 sec Solution 2 | Layered, 16% large fine fibers | 0.36 | 0.79 | 34 |
| Set I6 | (14 sec Solution 1 + 26 sec Solution 2) ×3 | Commingled, 16% large fine fibers | 0.36 | 0.79 | 32 |
| Set J | 30 sec Solution 1 + 90 sec Solution 2 | Layered, 20% large fine fibers | 0.38 | 0.81 | 32 |
| Set L | (10 sec Solution 1 + 30 sec Solution 2) ×3 | Commingled, 20% large fine fibers | 0.38 | 0.81 | 33 |
| Set M | 2 min Solution 2 only | 100% large fine fibers | 0.43 | 0.86 | 34 |

*Proportion of larger fine fibers (on a fiber count basis) was estimated from the diameters of small (Solution 1) and large (Solution 2) fine fibers, % solids in precursor spinning solutions, and syringe pump feed rates and spinning time, as described in the Fiber Proportion Calculation section, below.
** Derived from the Kirsch-Fuch equation

Method 6

**[0485]** A series of media samples including multiple layers having a variety of sizes of fine fibers were made. Samples included a base layer of large fine fibers, followed by a layer of small fine fibers, and topped by a layer of large fine fibers (Large/Small/Large, or L/S/L). Alternatively, samples included a base layer of large fine fibers, followed by a layer

Method 7:

**[0488]** A series of media samples including a base layer of large fine fibers and a commingled layer of small fine fibers and large fine fibers were also prepared.

**[0489]** First, a first fine fiber layer including large fine fibers (equivalent to 0.43 g/m$^2$ coverage) was deposited on a 0.2 mm thick, spunbond nylon scrim having a basis weight

of 70 g/m$^2$ and a solidity of 28% (Media Grade 23200, Cerex Advanced Fibers, Cantonment, Fla.) by spinning Solution 2 for 2 minutes at a pump rate of 0.075 mL/min. Next, a second fine fiber layer including commingled small fine fibers and large fine fibers was deposited by co-spinning two different electrospinning precursor solutions (Solution 1 and Solution 2) from two different syringes, delivered at the same pump rate (0.075 mL/minute) and for the same duration (either 2.5 minutes or 4.5 minutes).

**[0490]** All samples were subjected to a post-synthesis treatment to improve robustness via cross-linking. After electrospinning, formed fibers were thermally treated at 140° C. for 10 minutes.

Method 8:

**[0491]** First, a first fine fiber layer including large (1.4 μm diameter) fine fibers (equivalent to 0.54 g/m$^2$ coverage) was deposited on a 0.2 mm thick, spunbond nylon scrim having a basis weight of 70 g/m$^2$ and a solidity of 28% (Media Grade 23200, Cerex Advanced Fibers, Cantonment, Fla.) by spinning Solution 4 for 2 minutes at a pump rate of 0.075 mL/min.

**[0492]** Next, a mixed layer of fibers of different diameters (0.25 μm and 1.4 μm) was produced as described in Method 4 but using Solution 4 instead of Solution 2, according to the timing sequences in Table 1B. (Although the timing sequences of Table 1B are the same as the timing sequences of Table 1A, the resulting layers have different basis weights and proportions of fibers due to the substitution of Solution 4 for Solution 2).

Method 9:

**[0493]** First, a first fine fiber layer including large (1.4 μm diameter) fine fibers (equivalent to 0.54 g/m$^2$ coverage) was deposited on a 0.2 mm thick, spunbond nylon scrim having a basis weight of 70 g/m$^2$ and a solidity of 28% (Media Grade 23200, Cerex Advanced Fibers, Cantonment, Fla.) by spinning Solution 4 for 2 minutes at a pump rate of 0.075 mL/min.

**[0494]** Next, a mixed layer of fibers of different diameters (0.5 μm and 1.4 μm) were produced as described in Method 4 but using Solution 3 instead of Solution 1 and Solution 4 instead of Solution 2, according to the timing sequences in Table 1C. (Although the timing sequences of Table 1C are the same as the timing sequences of Table 1A, the resulting layers have different basis weights and proportions of fibers due to the substitution of Solution 3 for Solution 1 and Solution 4 for Solution 2).

TABLE 1B

| Pulsed electrospinning sequence | | | | | |
|---|---|---|---|---|---|
| Sample ID | Pulsed spinning sequence (2 minutes total duration) | Structure and composition* | Basis weight (g/m$^2$) (excluding large fine fiber support layer) | Basis weight (g/m$^2$) (all fine fibers) | % Solidity** |
| Set A | 2 min Solution 1 only | 100% small fine fibers | 0.22 | 0.76 | 35 |
| Set A5 | 102 sec Solution 1 + 18 sec Solution 4 | Layered, 1% large fine fibers | 0.27 | 0.81 | 36 |
| Set A6 | (51 sec Solution 1 + 9 sec Solution 4) ×2 | Commingled, 1% large fine fibers | 0.27 | 0.81 | 35 |
| Set B | 90 sec Solution 1 + 30 sec Solution 4 | Layered, 2% large fine fibers | 0.30 | 0.84 | 37 |
| Set D | (30 sec Solution 1 + 10 sec Solution 4) ×3 | Commingled, 2% large fine fibers | 0.30 | 0.84 | 33 |
| Set D5 | 72 sec Solution 1 + 48 sec Solution 4 | Layered, 4% large fine fibers | 0.35 | 0.89 | 37 |
| Set D6 | (18 sec Solution 1 + 12 sec Solution 4) ×4 | Commingled, 4% large fine fibers | 0.35 | 0.89 | 35 |
| Set E | 1 min Solution 1 + 1 min Solution 4 | Layered, 6.5% large fine fibers | 0.38 | 0.92 | 36 |
| Set I | (10 sec Solution 1 + 10 sec Solution 4) ×6 | Commingled, 6.5% large fine fibers | 0.38 | 0.92 | 36 |
| Set I5 | 42 sec Solution 1 + 78 sec Solution 4 | Layered, 11% large fine fibers | 0.43 | 0.97 | 39 |
| Set I6 | (14 sec Solution 1 + 26 sec Solution 4) ×3 | Commingled, 11% large fine fibers | 0.43 | 0.97 | 39 |
| Set J | 30 sec Solution 1 + 90 sec Solution 4 | Layered, 17% large fine fibers | 0.46 | 1.0 | 39 |
| Set L | (10 sec Solution 1 + 30 sec Solution 4) ×3 | Commingled, 17% large fine fibers | 0.46 | 1.0 | 40 |
| Set M | 2 min Solution 4 only | 100% large fine fibers | 0.54 | 1.08 | 42 |

*Proportion of larger fine fibers (on a fiber count basis) was estimated from the diameters of small (Solution 1) and large (Solution 4) fine fibers, % solids in precursor spinning solutions, and syringe pump feed rates and spinning time, as described in the Fiber Proportion Calculation section, below.

**Derived from the Kirsch-Fuch equation

TABLE 1C

| Pulsed electrospinning sequence | | | | | |
|---|---|---|---|---|---|
| Sample ID | Pulsed spinning sequence (2 minutes total duration) | Structure and composition* | Basis weight ($g/m^2$) (excluding large fine fiber support layer) | Basis weight ($g/m^2$) (all fine fibers) | Solidity** |
| Set A | 2 min Solution 3 only | 100% small fine fibers | 0.3 | 0.84 | 39 |
| Set B | 90 sec Solution 2 + 30 sec Solution 4 | Layered, 6.5% large fine fibers | 0.36 | 0.90 | 38 |
| Set D | (30 sec Solution 3 + 10 sec Solution 4) ×3 | Commingled, 6.5% large fine fibers | 0.36 | 0.90 | 38 |
| Set E | 1 min Solution 3 + 1 min Solution 4 | Layered, 17% large fine fibers | 0.42 | 0.96 | 41 |
| Set I | (10 sec Solution 3 + 10 sec Solution 4) ×6 | Commingled, 17% large fine fibers | 0.42 | 0.96 | 37 |
| Set J | 30 sec Solution 3 + 90 sec Solution 4 | Layered, 38% large fine fibers | 0.48 | 1.02 | 39 |
| Set L | (10 sec Solution 3 + 30 sec Solution 4) ×3 | Commingled, 38% large fine fibers | 0.48 | 1.02 | 38 |
| Set M | 2 min Solution 4 only | 100% large fine fibers | 0.54 | 1.08 | 41 |

*Proportion of larger fine fibers (on a fiber count basis) was estimated from the diameters of small (Solution 3) and large (Solution 4) fine fibers, % solids in precursor spinning solutions, and syringe pump feed rates and spinning time, as described in the Fiber Proportion Calculation section, below.
**Derived from the Kirsch-Fuch equation

Method 10

**[0495]** First, a first fine fiber layer including large (1.4 μm diameter) fine fibers (equivalent to 0.54 $g/m^2$ coverage) was deposited on a 0.2 mm thick, spunbond nylon scrim having a basis weight of 70 $g/m^2$ and a solidity of 28% (Media Grade 23200, Cerex Advanced Fibers, Cantonment, Fla.) by spinning Solution 4 for 2 minutes at a pump rate of 0.075 mL/min.

**[0496]** Next, a second fine fiber layer including commingled fine fibers of different diameters (0.25 μm and 1.4 μm) was deposited by co-spinning two different electrospinning precursor solutions (Solution 1 and Solution 4) from two different syringes, delivered at the same pump rate (0.075 mL/minute) and for the same duration (either 1 minute, 1.4 minutes, 2 minutes, 2.5 minutes, 3.6 minutes, or 4.5 minutes).

**[0497]** All samples were subjected to a post-synthesis treatment to improve robustness via cross-linking. After electrospinning, formed fibers were thermally treated at 140° C. for 10 minutes.

Method 11

**[0498]** First, a first fine fiber layer including large (1.4 μm diameter) fine fibers (equivalent to 0.54 $g/m^2$ coverage) was deposited on a 0.2 mm thick, spunbond nylon scrim having a basis weight of 70 $g/m^2$ and a solidity of 28% (Media Grade 23200, Cerex Advanced Fibers, Cantonment, Fla.) by spinning Solution 4 for 2 minutes at a pump rate of 0.075 mL/min.

**[0499]** Next, a second fine fiber layer including commingled fine fibers of different diameters (0.5 μm and 1.4 μm) was deposited by co-spinning two different electrospinning precursor solutions (Solution 3 and Solution 4) from two different syringes, delivered at the same pump rate (0.075 mL/minute) and for the same duration (either 2 minutes, 3 minutes, 4 minutes, or 5 minutes).

**[0500]** All samples were subjected to a post-synthesis treatment to improve robustness via cross-linking. After electrospinning, formed fibers were thermally treated at 140° C. for 10 minutes.

Method 12

**[0501]** A series of media samples including multiple layers having a variety of sizes of fine fibers were made. Samples included a base layer of large (1.4 μm diameter) fine fibers, followed by a layer of small (0.25 μm diameter) fine fibers, and topped by a layer of large (1.4 μm diameter) fine fibers (Large/Small/Large, or L/S/L). Alternatively, samples included a base layer of large (1.4 μm diameter) fine fibers, followed by a layer of small (0.25 μm diameter) fine fibers, then a layer of commingled small (0.25 μm diameter) fine fibers and large (1.4 μm diameter) fine fibers, and topped by a layer of large (1.4 μm diameter) fine fibers (Large/Small/Commingled/Large, or L/S/Commingled/L).

**[0502]** Large fine fibers (equivalent to 0.54 $g/m^2$ coverage) were deposited onto the scrim by spinning Solution 4 for 2 minutes. Without wishing to be bound by theory, it is believed the large fine fibers act as an underlying support layer for subsequent fiber layers. Next, a second layer of small fine fibers (equivalent to 0.22 $g/m^2$ coverage) was deposited by spinning Solution 1 for 2 minutes. If included, an intermediate (commingled) layer including both small fine fibers and large fine fibers was added by alternatingly ("pulsed") spinning from a syringe containing Solution 1 or Solution 4, for small fine fibers and large fine fibers, respectively, according to the timing sequences in Table 1B. Finally, a top layer of large fine fibers (equivalent to 0.54 $g/m^2$ coverage) was deposited by spinning Solution 4 for 2 minutes. All solutions were delivered at a pump rate of 0.075 mL/min.

**[0503]** All samples were subjected to a post-synthesis treatment to improve robustness via cross-linking. After electrospinning, formed fibers were thermally treated at 140° C. for 10 minutes.

Method 13

**[0504]** First, a first fine fiber layer including large (1.4 μm diameter) fine fibers (equivalent to 0.54 $g/m^2$ coverage) was deposited on a 0.2 mm thick, spunbond nylon scrim having a basis weight of 70 $g/m^2$ and a solidity of 28% (Media

Grade 23200, Cerex Advanced Fibers, Cantonment, Fla.) by spinning Solution 4 for 2 minutes at a pump rate of 0.075 mL/min.

**[0505]** Next, three additional layers of small fine fibers (each equivalent to 0.22 g/m$^2$ coverage) were deposited by spinning Solution 1 for 2 minutes three times.

**[0506]** Finally, a top layer of large fine fibers (equivalent to 0.54 g/m$^2$ coverage) was deposited by spinning Solution 4 for 2 minutes. All solutions were delivered at a pump rate of 0.075 mL/min.

**[0507]** All samples were subjected to a post-synthesis treatment to improve robustness via cross-linking. After electrospinning, formed fibers were thermally treated at 140° C. for 10 minutes.

Media Characterization

Scanning Electron Microscopy (SEM)

**[0508]** Samples were prepared for top-down SEM imaging by sputter-coating the surface with a gold and palladium mixture including an Au:Pd 60:40 mixture. Typically, a 5 kV or a 10 kV accelerating voltage was used and images were collected at ×500, ×1000 and x2500 magnifications with a secondary electron detector or a backscatter electron detector.

**[0509]** Samples were prepared for cross-sectional SEM imaging by preparing a 3 mm by 20 mm sample that included fine fiber on a support layer, typically placing the sample fine fiber side down in a weighing tin on a hard surface, filling the tin with liquid nitrogen to submerge the sample. After at least 30 seconds, a razor blade was used to cut the sample (while still submerged in liquid nitrogen) to expose a cross-section. After the cut was made and an additional 10-20 seconds had elapsed, the sample was removed from liquid nitrogen and mounted to SEM imaging. Samples were then sputter-coated with 60:40 Au:Pd. Typically, a 5 kV accelerating voltage was used and images were collected at ×1000 magnifications with a secondary electron detector.

Fiber Proportion Calculation Based on Spin Time

**[0510]** Relative amounts of small and large fine fibers (on a total fiber count basis) are determined using the following equation:

$$\%\ \text{Large Fibers} = 100 \times \frac{(V_L / D_L^2)}{((V_L / D_L^2) + (V_S / D_S^2))}$$

where $D_L$ and $D_S$ are diameters of the large fine fiber and small fine fibers, respectively; and $V_L$ and $V_S$ are volumes of the polymers comprising the large fine fiber and small fine fibers, respectively. Volumes, V, are calculated for small or large fine fiber according to:

$$V = \left(\% \frac{w}{v}\right) \times (\text{Pump Rate} \times \text{Spin Time}) \times \frac{1}{\rho}$$

where ρ is the density of the polymer comprising the small fine fibers or large fine fibers, and % w/v refer to the solids contents on a mass per volume basis of the polymer solutions.

Fiber Diameter

**[0511]** The fine fiber samples produced in Examples 1-7 had average fiber diameters no greater than 10 microns. Typically, the small fine fibers possessed average fiber diameters ranging from 200 nm to 600 nm, as measured by Scanning Electron Microscopy (SEM). Typically, the large fine fibers possessed average fiber diameters of at least 700 nm, as measured by Scanning Electron Microscopy (SEM). Fiber sizing was performed by imaging fibers via top-down SEM and measuring fiber diameter (or other dimensions of interest) in the resulting micrographs. Image processing software such as ImageJ, (FIJI Is Just ImageJ (FIJI), an updated version of ImageJ), and/or Trainable Weka Segmentation (an ImageJ plug-in) was used for fiber sizing. The diameter of the fiber was measured in at least 30 locations in the sample.

Fine Fiber Layer Thickness

**[0512]** The thickness of the fine fiber samples was measured by Scanning Electron Microscopy (SEM) via cross-sectional analysis of SEMs, prepared as described above. The thickness of the fine fiber layer in at least 5 images from different portions of the sample were determined using FIJI. Specifically, the top and bottom of the fine fiber layer were delineated using a polygon tool, the area outside the selected fine fiber cross-section was cleared, the area of the selected fine fiber cross-section was re-colored white using the threshold level tool to compensate for fibers on the borders of the selected section, and the maximum thickness in the image was measured and recorded. Five of these maximum values were rounded to the nearest tenth of a micron and then averaged to provide the thickness of the fine fiber sample.

Capillary Flow Porometry (Pore Size)

**[0513]** Capillary flow porometry (Porometer 3G micro, Through-Pore Size Analyzer, Quantachrome Instruments, Anton Paar, Boynton Beach, Fla.) measurements were performed to determine average maximum pore size, average mean flow pore size, and average minimum pore size based on three replicates for each sample.

**[0514]** Porofil Wetting Solution was used as a wetting fluid (Quantachrome Instruments, Anton Paar, Boynton Beach, Fla.). Samples 25 mm in diameter were subjected to a pressure sweep (that is, a continuous pressure scan) from 0.0256 bar to 1.275 bar in both wet and dry states (first wet, then dry) to determine pore sizes within 1 microns to 100 microns.

**[0515]** The sample was tested from low pressure to high pressure, while wet and dry. The air flow and sample pressure from the saturated part of the test is commonly called the wet curve. 256 data points were collected across the range of the scan of the pressures for both the dry curve and the wet curve. The test was performed at ambient conditions (for example, 20° C. to 25° C.). No empirical tortuosity factor and/or a shape factor was applied to adjust the pore size diameter definition.

**[0516]** The flow porometry test procedure collects a set of pressure (typically plotted on the x-axis) and air flow (typically plotted on the y-axis) data for the dry sample, and a set of pressure and air flow data for the saturated (wet) sample. These two sets of data are commonly called the dry curve and the wet curve. That is:

Dry Curve=$V_{dry}$=air flow through a dry sample as a function of pressure

Wet Curve=$V_{wet}$=air flow through a saturated sample as a function of pressure

**[0517]** Based on capillary theory, the pressure across the sample (ΔP) can be converted to pore diameter (d) using the Young-Laplace formula,

$$d = \frac{4\gamma\cos\theta}{\Delta P} \times (\text{Emperical Factor})$$

Where

**[0518]** γ=fluid surface tension

**[0519]** θ=fluid contact angle

**[0520]** d=pore diameter

**[0521]** ΔP=pressure across sample

**[0522]** This conversion allows the dry and wet curves to be defined as a function of pore diameter. That is:

Dry Curve=$V'_{dry}$=air flow through a dry sample as a function of diameter

Wet Curve=$V'_{wet}$=air flow through a saturated sample as a function of diameter

**[0523]** The cumulative flow pore size distribution (Q) is defined as the ratio of the wet curve over the dry curve as a function of pore diameter. Where,

$$Q(d) = \frac{V'_{wet}}{V'_{dry}}$$

**[0524]** The minimum pore size was calculated by determining the diameter at which the dry curve and the wet curve met.

**[0525]** The mean flow pore size was calculated at the pressure where the wet curve and the "half-dry" curve cross. The half-dry curve is obtained by the mathematical division by 2 of $V'_{dry}$.

**[0526]** The maximum pore size was determined by detecting the bubble point, where the bubble point was found after fluid begins passing through the sample, and three consecutive measurement increased by at least 1%. The bubble point is the value at the start of this sequence of three points.

Air Filtration Performance

**[0527]** Air filtration performance was assessed with a High-Efficiency Flat Sheet (HEFS) TSI Automated Filter Tester, Model 8127, test bench (TSI Incorporated, Shoreview, Minn.) to measure particle capture efficiency using 0.3 μm oil (bis(2-ethylhexyl) sebacate, Sigma-Aldrich) droplets (aerosol) at a flow rate of 14.7 liters per minute (L/min) to challenge 4 inch diameter media samples. TSI's CertiTest Model 8127 Automated Filter Tester is designed for testing filters, respirator cartridges, and filter media to the latest American government and industry-wide specification, and meets the standards of 42 CFR § 84 (Jun. 8, 1995).

Figure of Merit

**[0528]** Figure of Merit is a measure of the performance of a filter media and of the filter media's ability to provide a certain level of clarification of a stream with a minimum energy used. Larger Figure of Merit values are generally better than smaller values.

**[0529]** Figure of Merit (FOM) values were calculated from fractional penetration (P, the ratio of upstream and downstream counts), pressure drop (dP, inches $H_2O$) and face velocity (u, fpm):

$$FOM=(-\log_{10}P)/(dP/u)$$

**[0530]** Fractional penetration (P), pressure drop (dP) and face velocity (u) were measured using the HEFS TSI Automated Filter Tester, Model 8127, test bench, as described above.

Liquid Filtration Performance Testing

**[0531]** Liquid filtration performance was assessed with a Flatsheet, High-Accuracy, Singlepass Two-fluid (FHAST) bench. The FHAST bench includes a reservoir of hydraulic fluid that is loaded with particles of varying sizes, the particle-laden hydraulic fluid is then passed through the media, while the particle counts and sizes upstream of the media and downstream of the media are measured. The FHAST bench has the following features: flow rate control: 57 mL/min to 580 mL/min at ±2% error; temperature control: 25° C. to 40° C. at ±0.25° C. error; dP measurement: 0 psi to 25 psi at ±0.065% error; particle size: 1.7 μm to 20 μm; max particle concentration: 1,000,000/mL; dilution capabilities: 5:1-100:1. The FHAST bench was used in steady flow mode using ISO Medium Test Dust per ISO 11171:2016 at a concentration of 10 milligrams per liter (mg/L) in hydraulic fluid and at a flow rate of 0.347 L/min to challenge 2 inch diameter media samples. Values for media dP and efficiencies for a particular contaminant particle size (measured using commercially available particle counters, specifically PAMAS 4132 Particle Counting System for Liquids, calibrated with ISO Medium Test Dust per ISO 11171:2016, Hydraulic fluid power—Calibration of automatic particle counters for liquids) were collected at regular time intervals (approximately every 7 sec) throughout the duration of testing, which was terminated upon reaching a pre-set maximum media dP of 20 psi (measured with two Test Media dP sensors: (A) 0 psi to 5 psi, ±0.025% accuracy differential pressure transducer; high accuracy, low range dP sensor and (B) 0 psi to 25 psi, ±0.065% accuracy differential pressure transducer; low accuracy, high range dP sensor).

**[0532]** Beta ratio was evaluated under steady flow conditions (347 mL/min through a media sample 2 inches in diameter) using ISO 16889:2008 (Hydraulic fluid power—Filters—Multi-pass method for evaluating filtration performance of a filter element) except when testing flat sheet performance, the test was run in single-pass mode, instead of the multi-pass mode called for by the test standard. Hydraulic fluid (Mobil Aero HF, MIL-PRF-5606) was laden with ISO 12103-1 A3 Medium Test Dust (Powder Technology, Inc., Arden Hills, Minn.) at a concentration of 10 mg/L.

Instantaneous beta values were recorded every 7 seconds throughout the test duration. A test ends when a terminal dP of 20 psi is reached.

Solidity

**[0533]** Solidity (c) of a nonwoven layer (including, for example, a non-fine fiber layer or a composite including fine fiber and non-fine fiber layers) is calculated using the following equation:

$$c=BW/\rho Z$$

where BW is the basis weight, ρ is the density of the fiber, and Z is the thickness of the media.

**[0534]** Thickness was measured according to TAPPI T411 om-15, entitled "Thickness (caliper) of paper, paperboard, and combined board," and a foot pressure of 1.5 psi was used. Basis Weight was measured using TAPPI T410 om-08.

**[0535]** Because of the difficulty of measuring thickness of a fine fiber layer, solidity of a fine fiber layer is calculated using an adapted version of the Kirsch-Fuchs equation (see Kirsch et al., "Studies on Fibrous Aerosol Filters—III Diffusional Deposition of Aerosol in Fibrous Filter," *Ann. Occup. Hyg.* 1968; 11:299-304) using experimentally measured pressure drop values. Pressure drop (ΔP or dP) is determined using a FHAST bench, as described in the Liquid Filtration Performance Testing section, below.

**[0536]** First, the dimensionless fiber drag parameter $F^*_{1.0}$ is calculated from the following modified Kirsch-Fuchs equation:

$$\Delta P = \frac{4\left(\frac{BW}{\rho}\right)\mu U_\infty}{\pi D_f^2} F^*_{1.0}$$

where BW is basis weight, ρ is density of the fiber, μ is viscosity of the liquid (used for the pressure drop test), $U_\infty$ is velocity of the liquid through the media during the pressure drop test, and $D_f$ is effective fiber diameter. ΔP is determined from FHAST bench, as described in the Liquid Filtration Performance Testing section, below.

**[0537]** Second, solidity (c) is calculated from $F^*_{1.0}$ using the following equation:

$$F^*_{1.0}=4.3548e^{8.8822c}$$

**[0538]** For mixed fiber media, the effective fiber diameter accounts for the relative amounts of the small and large fibers, and is calculated from the following equation:

$$r_{eff} = \frac{\sum_{i=0}^{n} r_i^2 l_i}{\sum_{i=0}^{n} r_i l_i}$$

where $r_{eff}$ is the effective fiber radius, $r_i$ is the radius of fiber i, and $l_i$ is the fraction or relative amount of fiber i. Effective fiber diameter=$2r_{eff}$.

**[0539]** Basis weight of a fine fiber layer or layers is calculated as follows:

Total basis weight of the fine fiber layers=(mass of the fine fibers)/(area of scrim)

**[0540]** The mass of the fine fibers was calculated as follows:

Mass of fine fibers=(% w/v polymer in solution)×(pump rate)×(spinning time)

**[0541]** When the method of making the fine fiber is unknown, the mass of the fine fibers may be calculated as follows, after separating (for example, by peeling or delaminating) the fine fibers from the scrim or support:

Mass of fine fibers=(total mass of media sample)−(mass of bare scrim or support)

Example 1

**[0542]** Media was prepared according to Pendant Drop Sample Preparation Method 3, Table 1A, Set A (small fine fibers deposited directly on scrim) and Pendant Drop Sample Preparation Method 4, Table 1A, Set A (small fine fibers deposited on a large fine fiber layer deposited on scrim).

**[0543]** Media was tested as described in the Liquid Filtration Performance Testing section, above. Results are shown in FIG. **1**A and FIG. **1**C. The media including small fine fibers deposited directly on scrim (results shown in FIG. **1**A) had an initial pressure drop of 0.74 psi. The media including small fine fibers deposited on a large fine fiber layer deposited on scrim (results shown in FIG. **1**C) had an initial pressure drop of 0.75 psi.

**[0544]** An exemplary image of the large fine fiber layer deposited on scrim prior to small fine fibers being deposited on the large fine fiber layer is shown in FIG. **1**E.

**[0545]** SEM images of the resulting media are shown in FIG. **1**B (small fine fibers deposited directly on scrim) and FIG. **1**D (small fine fibers deposited on a large fine fiber layer deposited on scrim). Fiber "adjustment" and damage was observed in the small fine fibers deposited directly on scrim after testing (FIG. **1**B). No fiber "adjustment" or damage was observed in the small fine fibers deposited on a large fine fiber layer deposited on scrim (FIG. **1**D).

Example 2

**[0546]** Media was prepared according to Pendant Drop Sample Preparation Method 1. The resulting nonwoven had a theoretical basis weight of 1.64 g/m$^2$.

**[0547]** Control nonwoven media, prepared by co-spinning each single electrospinning precursor solution from two different syringes, had theoretical basis weights of 0.56 g/m$^2$ or 1.08 g/m$^2$, for Solution 1 and Solution 2, respectively.

**[0548]** SEM images of the resulting media are shown in FIG. **2**A. Features of the resulting media are shown in Table 2A.

**[0549]** The FOM values for these media samples for air filtration are shown in Table 2B. Comparison of the FOM values suggests that a media including commingled fibers of different diameters has improved performance (higher rejection of contaminants and lower pressure drop) compared to a media including small fine fibers alone (Table 2B).

**[0550]** Liquid filtration performance was assessed with a Flatsheet, High-Accuracy, Singlepass Two-fluid (FHAST) bench, as described herein. Similar β values were observed for media including commingled fibers and for media including small fine fibers alone (FIG. **2**B), but no benefit was observed with a media including commingled fibers in terms of reducing dP compared to a media including small fine fibers alone (FIG. **2**C). The liquid filtration performance

data (FIG. **2**B-FIG. **2**C) are consistent with porometry measurements (Table 2C) indicating that pore sizes of the media including commingled fibers are smaller compared to pore sizes for media including small fine fibers alone.

**[0551]** Without wishing to be bound by theory, it is believed that the media including commingled fibers failed to show any reduction in pressure drop compared to media including small fine fibers alone because the media including commingled fibers exhibited a higher total coverage of fibers compared to media including small fine fibers alone or media including large fine fibers alone. This difference in coverage is exemplified by the comparative basis weights: the media including commingled fibers had a basis weight (1.64 g/m$^2$) higher the basis weight of media including small fine fibers alone (0.56 g/m$^2$) or media including large fine fibers alone (1.08 g/m$^2$).

TABLE 2A

| Electrospinning Solution | Media | Initial dP on FHAST | Approximate Fiber Diameters | Exemplary image |
|---|---|---|---|---|
| | Cerex alone (bare scrim) | 0.3 psi | n/a | |
| Solution 1 | Cerex + Small Fine Fibers | 2.9 psi | 200-250 nm | FIG. 2A, left panel |
| Solution 1 + Solution 2 | Cerex + Commingled Fibers | 3.3 psi | (mixed) | FIG. 2A, central panel |
| Solution 2 | Cerex + Large Fine Fibers | 0.5 psi | 700-1000 nm | FIG. 2A, right panel |

TABLE 2B

Summary of FOM values as measured from HEFS

| Media | % Penetration | dP (mm $H_2O$) | FOM |
|---|---|---|---|
| Cerex alone | 98.7 | 0.7 | 13.8 |
| Large Fine Fibers | 84.7 | 2 | 60.7 |
| Commingled Fibers | 6.09 | 11.7 | 174.8 |
| Small Fine Fibers | 7.93 | 12.5 | 148.2 |

TABLE 2C

Summary of pore size measurements via capillary flow porometry

| Media | Max Pore Size (um) | Mean Flow Pore Size (um) | Min Pore Size (um) |
|---|---|---|---|
| Cerex alone | 66.4 ± 21.9 | 51.4 ± 12.1 | 29.1 ± 9.7 |
| Large Fine Fibers | 25.2 ± 3.3 | 16.2 ± 4.3 | 9.1 ± 0.1 |
| Commingled Fibers | 7.1 ± 1.2 | 3.4 ± 0.6 | 2.8 ± 0.5 |
| Small Fine Fibers | 9.4 ± 0.8 | 4.5 ± 0.7 | 2.5 ± 0.3 |

Example 3

**[0552]** Media was prepared according to Pendant Drop Sample Preparation Method 2 for a duration of 2 minutes, 3 minutes, or 5 minutes of electrospinning time. The resulting nonwovens had theoretical basis weights of 0.65 g/m$^2$, 0.98 g/m$^2$ and 1.63 g/m$^2$, respectively.

**[0553]** Control nonwoven media, prepared by co-spinning each single electrospinning precursor solution from two different syringes for 2 minutes, had theoretical basis weights of 0.44 g/m$^2$ and 0.86 g/m$^2$, for Solution 1 and Solution 2, respectively.

**[0554]** SEM images of the resulting media are shown in FIG. **3**

**[0555]** As noted in Example 1, an increase in basis weight was observed as a result of co-spinning electrospinning precursor solutions to form small fine fibers and large fine fibers. To accommodate for this increase in basis weight, control media samples of small fine fiber alone or large fine fibers alone, prepared by co-spinning from two syringes containing identical solutions were also analyzed.

**[0556]** Comparison of the FOM values for air filtration for the media samples prepared using a duration of 2 minutes of electrospinning suggests that a commingled fiber layer has improved performance (higher rejection of contaminants and lower pressure drop) compared to small fine fibers alone (Table 3A).

**[0557]** Interestingly, increasing fiber coverage (by prolonging electrospinning), even for commingled fiber media, led to an overall drop in FOM values due to a steep pressure drop. Liquid filtration performance was assessed with a Flatsheet, High-Accuracy, Singlepass Two-fluid (FHAST) bench, as described herein. Less pressure drop was observed for the commingled fiber media compared to small fine fibers alone (FIG. **3**D). However, comparison of β values (FIG. **3**F) indicates that these samples are operating in a trade-off regime wherein improvements in media dP come at a cost to efficiency. The performance of several commingled fiber media samples with different basis weights were also compared and it was observed that higher fiber coverage leads to increased efficiencies (FIG. **3**E) due to smaller pore sizes which, in turn, cause larger pressure drops (FIG. **3**G—comparing clean media dP). The FHAST bench results were in agreement with porometry measurements (see Table 3B), indicating that pore size highly correlates with the overall performance of a media sample. Moreover, maximum pore size and mean flow pore sizes depended on electrospinning duration (FIG. **3**H).

TABLE 3A

Summary of FOM values as measured from HEFS

| Media | % Penetration | dP (mm $H_2O$) | FOM |
|---|---|---|---|
| Cerex alone (bare scrim) | 98.7 | 0.7 | 13.8 |
| Large Fine Fibers, 2 min | 89.1 | 1.3 | 64.4 |
| Commingled Fibers, 2 min | 41.1 | 3.1 | 211.0 |
| Commingled Fibers, 3 min | 21.1 | 5.4 | 209.1 |
| Commingled Fibers, 5 min | 8.3 | 9.9 | 182.5 |
| Small Fine Fibers, 2 min | 37.3 | 4 | 177.7 |

TABLE 3B

Summary of pore size measurements via capillary flow porometry

| Media | Max Pore Size (um) | Mean Flow Pore Size (um) | Min Pore Size (um) | Basis Weight of the Fine fiber layer ($g/m^2$) |
|---|---|---|---|---|
| Cerex alone (bare scrim) | 66.4 ± 21.9 | 51.4 ± 12.1 | 29.1 ± 9.7 | 0.00 |
| Large Fine Fibers, 2 min | 33.0 ± 4.6 | 26.6 ± 5.6 | 23.0 ± 6.0 | 0.86 |
| Commingled Fibers, 2 min | 18.6 ± 9.1 | 9.1 ± 4.2 | 7.7 ± 3.9 | 0.65 |
| Commingled Fibers, 3 min | 8.8 ± 2.5 | 4.5 ± 1.2 | 3.8 ± 1.0 | 0.98 |
| Commingled Fibers, 5 min | 5.3 ± 1.7 | 2.6 ± 0.5 | 2.0 ± 0.3 | 1.63 |
| Small Fine Fibers, 2 min | 14.2 ± 4.2 | 6.7 ± 2.1 | 5.3 ± 1.4 | 0.44 |

Example 4

**[0558]** Media was prepared according to Pendant Drop Sample Preparation Method 3.

**[0559]** To impart a better degree of control over the fiber media structure and composition, a "pulsed" sequence (wherein small fine fibers and large fine fibers are deposited alternatingly onto the scrim support) was tested. In all cases, small fine fibers were deposited first, followed by large fine fibers to produce a series of layered fiber media samples with large fine fiber content varying from 2% to 20% (nominal values calculated using the equation described in the section Fiber Proportion Calculation based on Spin Time) on a fiber population basis.

**[0560]** This method allows the creation of different structures (including either layered or commingled fibers (see Table 1A)) to afford gradient or heterogeneous pore sizes. SEM imaging provided a visual confirmation of the ability to control media morphology.

**[0561]** FIG. **4** shows the incremental change in basis weight observed with increasing relative amounts of large fine fibers; a linear increase in basis weight was observed with up to 10% large fine fiber content.

Example 5

**[0562]** Media was prepared according to Pendant Drop Sample Preparation Method 4.

**[0563]** The resulting media included a "support layer" of large fine fibers (1 μm diameter) that was deposited prior to depositing a layer of commingled fiber diameter fibers.

**[0564]** As in Example 4, a "pulsed" sequence was used to deposit small fine fibers and large fine fibers alternatingly; however, in contrast to Example 4, a large fine fiber-modified scrim support was employed.

**[0565]** In all cases, in the second step of the procedure (that is, after the first fine fiber layer including large fine fibers had been deposited), small fine fibers were deposited first, followed by large fine fibers to produce a series of mixed fiber diameter media samples with large fine fiber content varying from 2% to 20% (nominal values calculated using the equation described in the section Fiber Proportion Calculation based on Spin Time) on a fiber population basis.

**[0566]** SEM imaging provided a visual confirmation of the ability to control media morphology (FIG. **5**A, FIG. **5**B). FIG. **5**A shows media including small fine fibers only (FIG. **5**A, panel A), media including layered fibers of mixed diameters (FIG. **5**A, panels A5, B, D5, E, I5, J), or media including large fine fibers only (FIG. **5**A, panel M). FIG. **5**B shows media including small fine fibers only (FIG. **5**B, panel A), media including commingled fibers of mixed diameters (FIG. **5**B, panels A6, D, D6, I, I6, L), or media including large fine fibers only (FIG. **5**B, panel M). The letters in each panel indicate the electrospinning sequence described in Table 1A.

**[0567]** Surprisingly, measured pore sizes for media samples of different composition only showed a weak correlation with the fraction of large fine fibers (see Table 4A and FIG. **5**C). These results suggest that, for samples with modest coverage of fibers (for example, 5 $g/m^2$), porometry tests fail to capture the presence of the gradient of pore sizes present in such media. Nevertheless, these data demonstrate that incorporation of large fine fibers within a network of small fine fibers may be effective at widening pore size distribution.

**[0568]** Comparing the performance in air filtration as measured by FOM values (see Table 4B) of mixed fiber diameter media structures having a layered fiber structure or a commingled fiber structure suggests that the structures have similar effects (see FIG. **5**D, lower panel). In general, both the layered fiber structure and the commingled fiber structure exhibit poorer performance as more of the small fine fibers (which impart efficiency) are replaced by large fine fibers. For a commingled fiber structure, there appears to be an optimal range of large fine fiber content (5%-7%) where FOM remains comparable to that of a purely small fine fiber network. In particular, a commingled fiber structure media sample retained a relatively high FOM (circle in FIG. **5**D, upper panel) despite its large pore size. However, FOM values and pore sizes do not seem to correlate well.

TABLE 4A

Summary of pore size measurements via capillary flow porometry

| | Max Pore Size (μm) | Mean Flow Pore Size (μm) | Min Pore Size (μm) |
|---|---|---|---|
| Cerex alone (bare scrim) | 65.1 ± 15.6 | 48.5 ± 10.0 | 23.6 ± 11.7 |
| Set A-100% Small Fine Fibers | 14.1 ± 1.5 | 6.6 ± 0.8 | 4.9 ± 1.6 |
| Set A5-2% Large Fine Fibers, Layered | 9.9 ± 3.9 | 5.4 ± 1.5 | 4.5 ± 1.2 |
| Set B-5% Large Fine Fibers, Layered | 15.1 ± 6.5 | 8.4 ± 3.3 | 6.9 ± 2.4 |
| Set D5-7% Large Fine Fibers, Layered | 11.8 ± 1.2 | 7.1 ± 0.8 | 6.3 ± 0.7 |
| Set E-10% Large Fine Fibers, Layered | 13.3 ± 0.5 | 9.2 ± 0.4 | 7.8 ± 0.7 |
| Set I5-16% Large Fine Fibers, Layered | 12.8 ± 3.5 | 7.5 ± 2.6 | 6.1 ± 1.8 |
| Set J-20% Large Fine Fibers, Layered | 13.6 ± 0.9 | 8.6 ± 1.5 | 6.9 ± 1.0 |
| Set A6-2% Large Fine Fibers, Commingled | 13.6 ± 1.6 | 7.2 ± 1.0 | 5.8 ± 0.8 |
| Set D-5% Large Fine Fibers, Commingled | 13.0 ± 1.6 | 8.2 ± 0.9 | 7.2 ± 0.9 |

TABLE 4A-continued

Summary of pore size measurements via capillary flow porometry

| | Max Pore Size (μm) | Mean Flow Pore Size (μm) | Min Pore Size (μm) |
|---|---|---|---|
| Set D6-7% Large Fine Fibers, Commingled | 18.9 ± 5.9 | 11.2 ± 2.4 | 7.5 ± 2.1 |
| Set I-10% Large Fine Fibers, Commingled | 11.8 ± 1.2 | 7.2 ± 0.5 | 5.9 ± 0.1 |
| Set I6-16% Large Fine Fibers, Commingled | 11.0 ± 1.8 | 7.0 ± 0.6 | 5.7 ± 0.6 |
| Set L-20% Large Fine Fibers, Commingled | 10.6 ± 0.6 | 7.3 ± 0.8 | 5.4 ± 0.6 |
| Set M-100% Large Fine Fibers | 14.2 ± 0.7 | 11.2 ± 0.6 | 9.6 ± 0.8 |

TABLE 4B

Summary of FOM values as measured from HEFS

| Media | % Penetration | dP (mm $H_2O$) | FOM |
|---|---|---|---|
| Bare Cerex | 98.7 | 0.7 | 14 |
| Set A-100% Small Fine Fibers | 41.6 | 4.1 | 155 |
| Set A5-2% Large Fine Fibers, Layered | 45.7 | 3.9 | 146 |
| Set B-5% Large Fine Fibers, Layered | 45.2 | 3.8 | 152 |
| Set D5-7% Large Fine Fibers, Layered | 56.3 | 3.2 | 130 |
| Set E-10% Large Fine Fibers, Layered | 56.3 | 3.1 | 135 |
| Set I5-16% Large Fine Fibers, Layered | 59.2 | 3.3 | 115 |
| Set J-20% Large Fine Fibers, Layered | 65.8 | 3.0 | 101 |
| Set A6-2% Large Fine Fibers, Commingled | 77.6 | 2.8 | 65 |
| Set D-5% Large Fine Fibers, Commingled | 41.6 | 4.1 | 155 |
| Set D6-7% Large Fine Fibers, Commingled | 45.2 | 3.9 | 148 |
| Set I-10% Large Fine Fibers, Commingled | 46.3 | 3.7 | 150 |
| Set I6-16% Large Fine Fibers, Commingled | 54.1 | 3.1 | 143 |
| Set L-20% Large Fine Fibers, Commingled | 58.9 | 3.1 | 125 |
| Set M-100% Large Fine Fibers | 63.8 | 2.8 | 116 |

**[0569]** Importantly, providing a support layer of large fine fibers for a layer or layers including fibers of mixed fiber diameters eliminated the β collapse observed in media that included the same layer or layers of mixed fiber diameters but did not include such a support layer of large fine fibers. An exemplary comparison is shown in FIG. **5**E and FIG. **5**F. FIG. **5**E shows a commingled layer of mixed fiber diameters (including 5% large fine fibers), prepared as described in Method 3, Table 1A, Set B, the commingled layer having a basis weight of 0.71 g/m$^2$ and the support layer and the commingled layer having an initial pressure drop (dP) of 0.48 psi. FIG. **5**F shows a commingled layer of mixed fiber diameters (including 5% large fine fibers) deposited on a support layer of large fine fibers (the large fine fibers having a basis weight of 0.43 g/m$^2$), prepared as described in Method 4, Table 1A, Set B, the commingled layer having a basis weight of 0.71 g/m$^2$, and support layer and the two fine fiber layers having an initial pressure drop (dP) of 0.77 psi.

**[0570]** Moreover, as shown in FIG. **5**G-FIG. **5**J, media including fibers of mixed fiber diameters having 5%-7% large fine fiber content exhibited a similar efficiency to a media layer including small fine fibers alone while exhibiting a slight improvement in pressure drop. Similar trends were observed in mixed fiber diameter media structures having a layered structure and in mixed fiber diameter media structures having a commingled fiber structure. In contrast, in media having greater than 10% large fine fiber media content, the decrease in pressure drop was accompanied by a decrease in efficiency. (See FIG. **5**G-FIG. **5**J and FIG. **5**K.) Without wishing to be bound by theory, it is believed that the increasing amounts of large fine fibers in a media including fibers of mixed fiber diameters "open up" the fine fiber structure.

Example 6

**[0571]** Media samples were prepared according to Method 5 which includes depositing a layer of large fine fibers as a support layer (having a basis weight of at least 0.43 g/m$^2$) underneath a network of small fine fibers (having a basis weight of 0.09 g/m$^2$, 0.10 g/m$^2$, 0.22 g/m$^2$, 0.31 g/m$^2$, 0.45 g/m$^2$, or 0.56 g/m$^2$). Pressure drop and over-all β values were tested. Results are shown in FIG. **6**B-FIG. **6**C.

**[0572]** An exemplary SEM image wherein the top layer of small fine fibers are covering the underlying network of supporting large fine fibers is shown in FIG. **6**A.

**[0573]** Media including a layer of small fine fibers at a range of basis weights exhibited good efficiency with low pressure drop.

Example 7

**[0574]** Media samples prepared according to Method 6. The media included a first fine fiber layer of large fine fibers, followed by small fine fibers, then a layer of commingled small fine fibers and large fine fibers, and, finally, by a layer of large fine fibers (referred to as Large/Small/Commingled/Large, or L/S/Commingled/L). Alternatively, an interior layer of commingled fibers (between the two layers of large fine fibers) was deposited by electrospinning as described in Table 1A. Pressure drop and over-all β values were assessed with a Flatsheet, High-Accuracy, Singlepass Two-fluid (FHAST) bench, as described herein. Exemplary images are shown in FIG. **7**A-FIG. **7**B. Results are shown in FIG. **7**C-FIG. **7**D.

**[0575]** It is believed that including mixed small and large diameter fiber layers between large fine fiber layers will be particularly useful for maintaining the structural integrity of intermediate layers in applications that require back-pulsing for media cleaning/regeneration.

Example 8

**[0576]** Media samples were prepared according to Method 7 and included a layer of large fine fibers (having a basis weight of at least 0.43 g/m$^2$) underneath a layer of commingled small fine fibers and large fine fibers. Samples were compared with media samples were prepared according to Method 5 (a layer of large fine fibers underneath a network of small fine fibers).

**[0577]** The layer of commingled small and large fine fibers includes approximately 10% large fine fibers on a total number of fibers basis, wherein the percentage was estimated from the diameters of small and large fine fibers, percent solids in precursor spinning solutions, syringe pump feed rates, and electrospinning time. The layer of commingled small fine fibers and large fine fibers was prepared by either approximating the basis weight of the second

(small fine fiber) layer of a media prepared using Method 5 or by approximating the total number of fibers in the second (small fine fiber) layer of a media prepared using Method 5. As shown in Table 5A, the resulting media layers had resulting basis weights of 0.82 g/m$^2$ and 1.47 g/m$^2$, whereas the second (small fine fiber) layer of a media prepared using Method 5 had a basis weight of 0.56 g/m$^2$.

**[0578]** Pressure drop and overall β values of the resulting media were tested. Results are shown in FIG. **8**B-FIG. **8**C. A representative SEM image is shown in FIG. **8**A.

TABLE 5A

Summary of FOM values as measured from HEFS

| Media | Basis weight of the second fine fiber layer | % Penetration | dP (mm $H_2O$) | FOM |
|---|---|---|---|---|
| Cerex alone | | 98.7 | 0.7 | 13.8 |
| Commingled Fibers (Method 7) | 0.82 g/m$^2$ | 32.7 | 5.3 | 154 |
| Commingled Fibers (Method 7) | 1.47 g/m$^2$ | 22.1 | 7.9 | 138 |
| Small Fine Fibers (Method 5) | 0.56 g/m$^2$ | 20.7 | 8 | 149 |

TABLE 5B

Summary of pore size measurements via capillary flow porometry

| Media | Max Pore Size (um) | Mean Flow Pore Size (um) | Min Pore Size (um) |
|---|---|---|---|
| Cerex alone | 66.4 ± 21.9 | 51.4 ± 12.1 | 29.1 ± 9.7 |
| Commingled Fibers | 4.9 ± 1.0 | 2.7 ± 0.8 | 2.1 ± 0.3 |
| Commingled Fibers | 3.9 ± 1.4 | 1.8 ± 0.8 | 1.6 ± 0.7 |
| Small Fine Fibers | 2.7 ± 1.2 | 1.7 ± 0.4 | 1.5 ± 0.4 |

**[0579]** The introduction of commingled large fine fibers within the network of small fine fibers increased pore sizes relative to layers including small fine fibers alone, despite the higher basis weight observed for those layers (see Table 5B).

**[0580]** Evaluation of air filtration performance via HEFS bench testing was consistent with the pore size results, in that lower pressure drops were achieved than with small fine fibers alone while maintaining the Figure of Merit (FOM) (see Table 5A, Commingled Fibers of 0.82 g/m$^2$ basis weight vs Small Fine Fibers with comparable FOM of ~150).

**[0581]** Liquid filtration performance was assessed with a Flatsheet, High-Accuracy, Singlepass Two-fluid (FHAST) bench, as described herein. A significant improvement in media dP (FIG. **8**A) was observed for co-spun samples compared to a large fine fiber-supported network of small fine fibers. However, there was a trade-off in efficiencies such that for these media with commingled small fine fibers and large fine fibers a β of 1000 was achieved only for >5 micron contaminant particles (compared to a β of 1000 for >3 micron particles for the non-commingled small fine fibers alone). Overall, the media consisting of commingled small and large fine fibers with an underlying support layer of large fine fibers exhibited good efficiency with low pressure drop.

## Example 9—Comparison with Fine Glass Fiber Containing Media

**[0582]** The filter media of Example 5 were compared against two liquid media products containing fine glass fibers. The first glass media has a β rating of 1,000 for particles <4 μm; the second has a β rating of 1,000 for particles >5 μm. Similar products are commercially available from Lydall, Inc. (Manchester, Conn.) and include, respectively, LyPore Grade 9428 and LyPore Grade 9221. Results are shown in FIG. **5**G-FIG. **5**J and Table 6.

**[0583]** The two liquid media products including fine glass fibers tested had higher initial pressure drop, resulting from the thicknesses of these glass fiber-containing media, which in turn allows for some extent of depth loading. All samples including a large fine fiber content of up to 10% had comparable (if not slightly better) efficiencies to glass media rated $\beta_{5\ um}$=1,000, particularly for contaminants up to 5 μm in size. Improvements in media dP and efficiencies, benchmarked against a glass fiber media having a β rating of 1,000 for particles >5 μm, are summarized in Table 6A.

**[0584]** Comparisons for these two performance metrics against a media including small fine fibers alone (but supported by large fine fibers) are summarized in Table 6B.

**[0585]** The media of Example 6 were also compared against a liquid media product including fine glass fibers having a β rating of 1,000 for particles <4 μm. The media of Example 6 surpassed the efficiency of the glass fiber media having a β rating of 1,000 for particles <4 μm and exhibited significantly lower pressure drop (see FIG. **6**A-FIG. **6**B).

TABLE 6A

Comparison with glass fiber media (β = 1000 for > 5 μm particles) of initial pressure drop (dP) and over-all β values for 3 μm and 5 μm particles

| Media | Clean Media dP (psi) | % Improvement* | Over-all β (3 μm) | % Improvement* | Over-all β (5 μm) | % Improvement* |
|---|---|---|---|---|---|---|
| glass fiber media (β = 1000 for > 5 μm particles) | 1.63 | — | 25 | — | 125 | — |
| COMMINGLED SMALL AND LARGE FINE FIBERS | | | | | | |
| Set A-100% | 0.75 | 54 | 55 | 116 | 222 | 78 |
| Set A6-2% | 0.84 | 48 | 58 | 128 | 188 | 51 |
| Set D-5% | 0.65 | 60 | 34 | 32 | 112 | (−11) |
| Set D6-7% | 0.56 | 66 | 20 | (−23) | 63 | (−49) |
| Set I-10% | 0.71 | 56 | 29 | 15 | 94 | (−25) |

TABLE 6A-continued

Comparison with glass fiber media (β = 1000 for > 5 μm particles) of initial pressure drop (dP) and over-all β values for 3 μm and 5 μm particles

| Media | Clean Media dP (psi) | % Improvement* | Over-all β (3 μm) | % Improvement* | Over-all β (5 μm) | % Improvement* |
|---|---|---|---|---|---|---|
| LAYERED SMALL AND LARGE FINE FIBERS | | | | | | |
| Set A5-2% | 0.81 | 50 | 64 | 153 | 234 | 88 |
| Set B-5% | 0.84 | 48 | 65 | 157 | 237 | 90 |
| Set D5-7% | 0.71 | 56 | 33 | 29 | 117 | (−6) |
| Set E-10% | 0.65 | 60 | 29 | 15 | 88 | (−29) |

*Percent (%) Improvement is reported against glass fiber media (β = 1000 for > 5 μm particles as [(Sample value − Glass Media value)/Glass Media value]×100; negative signs and parentheses indicate inferior performance

TABLE 6B

Comparison of initial pressure drop (dP) and over-all efficiencies (β values) for 3 and 5 μm particles (versus Set A-100% small fine fibers supported by a layer of large fine fibers)

| 07162019 Media | Clean Media dP (psi) | % Improvement* | Over-all β (3 μm) | % Improvement* | Over-all β (5 μm) | % Improvement* |
|---|---|---|---|---|---|---|
| Set A-100% | 0.75 | — | 55 | — | 222 | — |
| COMMINGLED SMALL AND LARGE FINE FIBERS | | | | | | |
| Set A6-2% | 0.84 | (−12) | 58 | 6 | 188 | (−15) |
| Set D-5% | 0.65 | 13 | 34 | (−39) | 112 | (−50) |
| Set D6-7% | 0.56 | 25 | 20 | (−64) | 63 | (−72) |
| Set 1-10% | 0.71 | 5 | 29 | (−46) | 94 | (−58) |
| LAYERED SMALL AND LARGE FINE FIBERS | | | | | | |
| Set A5-2% | 0.81 | (−8) | 64 | 17 | 234 | 6 |
| Set B-5% | 0.84 | (−12) | 65 | 19 | 237 | 7 |
| Set D5-7% | 0.71 | 5 | 33 | (−40) | 117 | (−47) |
| Set E-10% | 0.65 | 13 | 29 | (−47) | 88 | (−60) |

**[0586]** The media of Example 7 were also compared against a liquid media product including fine glass fibers having a β rating of 1,000 for particles <4 μm. Notably, samples wherein the commingled layer included up to 5% large fine fiber content were also able to match efficiencies of efficiency of glass fiber media having a β rating of 1,000 for particles <4 μm for contaminant particles of up to 3 μm (FIG. 7A-FIG. 7B).

Example 10

**[0587]** To further examine the interplay between the fiber diameter of the first fine fiber layer, the thickness of the fine fiber layers, and the average maximum pore size of the composite, the ability of the samples of Examples 1 to 8 to withstand Liquid Filtration Performance Testing was measured. As used in this Example, the "composite" refers to any layers of fine fiber (including, for example, the first, second, etc., layers of fine fibers) and the support layer. The composite includes at least one layer of fine fiber.

**[0588]** For each sample tested, the ratio of the total fine fiber basis weight to the average maximum pore size of the composite was plotted against the basis weight of the second layer of fine fibers.

**[0589]** In FIG. **11**, the x axis shows the basis weight of the second layer of fine fibers; the y axis shows

$$\frac{\text{total basis weight of fine fibers}}{\text{maximum pore size of the over-all composite}}.$$

As used herein the "total basis weight of fine fibers" is the basis weight of any fine fiber layers (including, for example, the first, second, etc., layers of fine fibers).

**[0590]** Because the pore size within a fine fiber layer depends on multiple factors such as fine fiber diameter, solidity, and uniformity, and because the basis weight of the fine fibers reflects fiber diameter, solidity, and uniformity, a ratio of the total basis weight of the fine fibers to the average maximum pore size values of the composite was used to normalize the pore size values.

**[0591]** Total basis weight of the fine fiber layers was calculated as follows:

Total basis weight of the fine fiber layers=(mass of the fine fibers)/(area of scrim)

**[0592]** The mass of the fine fibers was calculated as follows:

Mass of fine fibers=(% w/v polymer in solution)×(pump rate)×(spinning time)

**[0593]** When the method of making the fine fiber is unknown, the mass of the fine fibers may be calculated as follows, after separating (for example, by peeling or delaminating) the fine fibers from the scrim or support:

Mass of fine fibers=(total mass of media sample)−(mass of bare scrim or support)

**[0594]** Plotting the ratio of the basis weight versus a maximum pore size of the composite against the basis weight of the second layer of fine fibers allows the identification of the features (fine fiber basis weight and maximum pore size of the composite) that correlated with a fine fiber layer likely to experience damage during FHAST bench testing. As shown in FIG. **11**, samples that withstood Liquid Filtration Performance Testing were distinguished from with samples that did not withstand Liquid Filtration Performance Testing and exhibited damage to the fine fiber structure, visible using SEM imaging, and/or β collapse.

**[0595]** A dashed line indicates the slope of a line expected to delineate composites that can withstand Liquid Filtration Performance Testing and are unlikely to suffer fiber damage during use of a filtration layer, from composites that are likely to suffer fiber damage during use of a filtration layer. The dotted line in FIG. **11**B indicates the properties of a trendline having a similar slope. Circular data points located below the dashed line correspond to media samples where a first layer of large fine fiber was deposited as described in Methods 4, 5, 6 and 7.

Example 11

**[0596]** Sample integrity of composite samples during FHAST bench testing up to 20 psi (at 0.56 feet/minute face velocity, as further described in the Liquid Filtration Performance Testing methods) was evaluated and initial pressure drop of each composite was plotted against composite average maximum pore size and the composite average mean flow pore size. As used in this Example, the "composite" refers to any layers of fine fiber (including, for example, the first, second, etc., layers of fine fibers) and the support layer. The composite includes at least one layer of fine fiber.

**[0597]** Composite maximum pore size and composite mean flow pore size for each sample was measured by flow porometry, and three measurements were averaged to obtain composite average maximum pore size and composite average mean flow pore size. Each sample included mixed diameter fine fibers and a substrate. Some samples included a layer of fine fibers that included "large" fine fibers and "small" fine fibers, prepared as described in Methods 1, 2 or 3. Some samples included a first layer of fine fibers and a second layer of fine fibers where the first layer of fine fibers included fine fibers having an average diameter at least three times the average fiber diameter of the smallest fibers of the second fine fiber layer, prepared as described in Methods 4, 5, 6 or 7.

**[0598]** Results are shown in FIG. **12**. Triangles represent samples that maintained fine fiber structural integrity throughout FHAST bench testing; squares represent samples that suffered from fine fiber blow-out during FHAST bench testing (indicated by beta collapse). Samples that included two fine fiber layers, the first layer including fine fibers having an average diameter at least three times the average fiber diameter of the smallest fibers of the second fine fiber layer are indicated by filled shapes. Samples that included one fine fiber layer including mixed diameter fibers are indicated by un-filled shapes.

**[0599]** Most of the media samples having only one layer of fine fibers (that is, that were prepared using Methods 1, 2 or 3), exhibited fine fiber damage (represented by open squares).

**[0600]** A few media samples having only one layer of fine fibers survived up to 20 psi during FHAST bench testing layer (represented by open triangles). Without wishing to be bound by theory, it is believed these fine fiber layers survived testing because the coverage (basis weight) was very high—but such high basis weight comes at the cost of higher initial pressure drop.

**[0601]** In contrast, all of the media samples that were prepared using Methods 4, 5, 6 or 7, and included two fine fiber layer maintained fine fiber structural integrity (represented by filled triangles).

**[0602]** The results illustrate that composite average maximum pore size (FIG. **12**A) and composite average mean flow pore size (FIG. **12**B) both correlate with the ability of the composite to withstand FHAST bench testing—a laboratory test that highly correlates with the ability of the composite to withstand at least 20 psi pressure drop during liquid filtration, indicating better filter performance than a filter media that cannot withstand the same conditions.

**[0603]** While some media samples having a composite average maximum pore sizes as large as 20 μm withstood FHAST bench testing, a transition zone where some media samples begin to fail testing was observed for media samples having a composite average maximum pore sizes between 14 μm and 20 μm.

**[0604]** Similarly, while some media have a composite average mean flow pore size as large as 11 μm withstood FHAST bench testing, a transition zone where some media samples begin to fail testing was observed for media samples having a composite average maximum pore sizes between 6 μm and 11 μm.

**[0605]** For example, a sample without a large fine fiber support having a composite average maximum pore size of 11 μm is unable to survive FHAST bench testing, while a sample with a large fine fiber support having a composite average maximum pore size of 11 μm is able to survive FHAST bench testing. Being able to use a fine fiber sample with a larger pore size allows the fine tuning of efficiency without a detrimental pressure drop of the resulting composite.

Example 12A

**[0606]** Media samples were prepared according to Method 8 and included a layer of large fine fibers (having a basis weight of at least 0.54 $g/m^2$) underneath a layer of commingled fibers of mixed diameters (0.25 μm fibers and 1.4 μm fibers).

**[0607]** SEM imaging provided a visual confirmation of the ability to control media morphology (FIG. **13**A, FIG. **13**B). FIG. **13**A shows media including small fine fibers only (FIG. **13**A, panel A), media including layered fibers of mixed diameters (FIG. **13**A, panels A5, B, D5, E, I5, J), or media including large fine fibers only (FIG. **13**A, panel M). FIG. **13**B shows media including small fine fibers only (FIG. **13**B,

panel A), media including commingled fibers of mixed diameters (FIG. **13**B, panels A6, D, D6, I, I6, L), or media including large fine fibers only (FIG. **13**B, panel M). The letters in each panel indicate the electrospinning sequence described in Table 1B.

**[0608]** Composite maximum pore size, mean flow pore size, and minimum pore size for each sample were measured by capillary flow porometry. Results are shown in Table 7A. A comparison of pore sizes for commingled mixed diameter fine fiber structures and layered mixed diameter fine fiber structures are shown in FIG. **13**C.

**[0609]** Pressure drop (dP) values are shown in FIG. **13**D (Set A, Set A5, Set B, Set D5, Set E, Set 15, Set J, and Set M of Table 1B) and FIG. **13**E (Set A, Set A6, Set D, Set D6, Set I, Set I6, Set L, and Set M of Table 1B); the plots also show values for comparative liquid media products including fine glass fibers having a β rating of 1,000 for particles <4 μm or having a β rating of 1,000 for particles <5 μm. Efficiency values (over-all β ratings) are shown in 13F (Set A, Set A5, Set B, Set D5, Set E, Set I5, Set J, and Set M of Table 1B) and FIG. **13**G (Set A, Set A6, Set D, Set D6, Set I, Set I6, Set L, and Set M of Table 1B); the plots also show values for comparative liquid media products including fine glass fibers having a β rating of 1,000 for particles <4 μm or having a β rating of 1,000 for particles <5 μm.

**[0610]** As shown in FIG. **13**D-FIG. **13**G, media including fibers of mixed fiber diameters having 1% large fine fiber content exhibited a similar efficiency to a media layer including small fine fibers alone while exhibiting a significant improvement in pressure drop. In contrast, in media having greater than 5% large fine fiber media content, the decrease in pressure drop was accompanied by a decrease in efficiency. (See FIG. **13**E and FIG. **13**G.) Without wishing to be bound by theory, it is believed that the increasing amounts of large fine fibers in a media including fibers of mixed fiber diameters "open up" the fine fiber structure.

Example 12B

**[0611]** Media samples were prepared according to Method 10 and included a layer of large fine fibers (having a basis weight of at least 0.54 g/m$^2$) underneath a layer of commingled 0.25 μm fibers and 1.4 μm fibers.

**[0612]** Resulting media included a commingled fine fiber layer having a basis weight of 0.38 g/m$^2$, 0.53 g/m$^2$, 0.76 g/m$^2$, 0.95 g/m$^2$, 1.37 g/m$^2$, or 1.71 g/m$^2$ (for precursor solutions delivered for 1 minute, 1.4 minutes, 2 minutes, 2.5 minutes, 3.6 minutes, or 4.5 minutes, respectively). The commingled fine fiber layer included 6.5% large (1.4 μm diameter) fiber content on fiber count basis. Basis weights and calculated solidities are shown in Table 7C.

**[0613]** Composite maximum pore size, mean flow pore size, and minimum pore size for each sample were measured by capillary flow porometry. Results are shown in Table 7B and FIG. **13**H.

**[0614]** FIG. **13**C (see Example 12A) shows that for samples having the same basis weight and relative amounts of small and large fibers (for example Set I in Table 1B of 0.38 g/m$^2$ supported fibers of 6.5% large fiber content vs the first row in Table 7B), commingling of small and large fibers significantly "opens up" the fine fiber structure as evidenced by the increase in pore sizes. FIG. **13**H shows an over-all trend of decreasing pore sizes with increasing commingled fiber coverage, with more pronounced pore size reductions as the basis weight is increased from 0.38 to 0.53 g/m$^2$.

**[0615]** Pressure drop (dP) values are shown in FIG. **13**I, and efficiency values (over-all β ratings) are shown in FIG. **13**J.

Example 12C

**[0616]** Media samples were prepared according to Method 12 and included a base layer of large (1.4 μm diameter) fine fibers, followed by a layer of small (0.25 μm diameter) fine fibers, then a layer of commingled small (0.25 μm diameter) fine fibers and large (1.4 μm diameter) fine fibers, and topped by a layer of large (1.4 μm diameter) fine fibers (Large/Small/Commingled/Large, or L/S/Commingled/L). Basis weights and solidity are shown in Table 7D.

**[0617]** Pore sizes for L/S/Commingled/L media were measured, and results are shown in FIG. **13**K.

**[0618]** Resulting pressure drop (dP) values are shown in FIG. **13**L, and efficiency values (over-all β ratings) are shown in FIG. **13**M.

TABLE 7D

Summary of basis weight and calculated solidity

| | Basis Weight | Solidity** |
|---|---|---|
| 100% small | 0.22 g/m$^2$ | 37 |
| Commingled 2% Large | 0.30 g/m$^2$ | 37 |
| Commingled 4% Large | 0.35 g/m$^2$ | 37 |
| Commingled 6.5% Large | 0.38 g/m$^2$ | 36 |
| Commingled 11% Large | 0.43 g/m$^2$ | 35 |
| Commingled 17% Large | 0.46 g/m$^2$ | 40 |
| 100% Large | 0.54 g/m$^2$ | 39 |

**Derived from the Kirsch-Fuch equation

TABLE 7A

Summary of pore size measurements via capillary flow porometry

| | Max Pore Size (μm) | Mean Flow Pore Size (μm) | Min Pore Size (μm) |
|---|---|---|---|
| Cerex alone (bare scrim) | 65.1 ± 15.6 | 48.5 ± 10.0 | 23.6 ± 11.7 |
| Set A-100% Small Fine Fibers | 6.2 ± 2.5 | 3.4 ± 0.5 | 3.2 ± 0.4 |
| Set A5-1% Large Fine Fibers, Layered | 7.4 ± 2.8 | 3.8 ± 0.8 | 3.5 ± 0.7 |
| Set B-2% Large Fine Fibers, Layered | 7.3 ± 2.5 | 3.3 ± 0.7 | 2.9 ± 0.5 |
| Set D5-4% Large Fine Fibers, Layered | 9.0 ± 5.5 | 3.8 ± 1.0 | 3.4 ± 0.7 |
| Set E-6.5% Large Fine Fibers, Layered | 4.9 ± 2.1 | 3.4 ± 1.2 | 3.1 ± 0.9 |
| Set I5-11% Large Fine Fibers, Layered | 6.7 ± 0.6 | 4.4 ± 0.4 | 3.9 ± 0.2 |
| Set J-17% Large Fine Fibers, Layered | 10.5 ± 1.5 | 6.1 ± 0.6 | 5.4 ± 0.5 |
| Set A6-1% Large Fine Fibers, Commingled | 5.3 ± 3.0 | 3.3 ± 1.2 | 2.9 ± 1.0 |
| Set D-2% Large Fine Fibers, Commingled | 8.2 ± 1.0 | 4.6 ± 1.1 | 4.0 ± 0.9 |
| Set D6-4% Large Fine Fibers, Commingled | 9.6 ± 2.8 | 4.6 ± 0.9 | 4.1 ± 0.8 |
| Set I-6.5% Large Fine Fibers, | 10.3 ± 2.5 | 4.8 ± 0.6 | 4.2 ± 0.6 |

TABLE 7A-continued

Summary of pore size measurements via capillary flow porometry

| | Max Pore Size (μm) | Mean Flow Pore Size (μm) | Min Pore Size (μm) |
|---|---|---|---|
| Commingled Set I6-11% Large Fine Fibers, | 7.2 ± 0.9 | 4.7 ± 0.6 | 4.2 ± 0.7 |
| Commingled Set L-17% Large Fine Fibers, | 8.2 ± 0.9 | 4.8 ± 0.2 | 4.3 ± 0.2 |
| Commingled Set M-100% Large Fine Fibers | 11.8 ± 1.2 | 6.9 ± 0.5 | 6.0 ± 0.4 |

TABLE 7B

Summary of pore size measurements via capillary flow porometry.

| | Max Pore Size (μm) | Mean Flow Pore Size (μm) | Min Pore Size (μm) |
|---|---|---|---|
| Commingled-0.38 g/m$^2$ | 17.3 ± 2.7 | 9.2 ± 3.3 | 6.3 ± 3.1 |
| Commingled-0.53 g/m$^2$ | 9.1 ± 3.3 | 5.0 ± 2.1 | 4.2 ± 1.8 |
| Commingled-0.76 g/m$^2$ | 7.7 ± 4.1 | 4.7 ± 2.0 | 3.9 ± 1.4 |
| Commingled-0.95 g/m$^2$ | 8.3 ± 1.9 | 5.4 ± 1.0 | 4.7 ± 0.9 |
| Commingled-1.37 g/m$^2$ | 4.8 ± 2.2 | 3.4 ± 1.4 | 3.0 ± 1.1 |
| Commingled-1.71 g/m$^2$ | 1.9 ± 0.4 | 1.5 ± 0.3 | 1.4 ± 0.2 |

TABLE 7C

Summary of basis weight and calculated solidity

| | Basis Weight | Solidity** |
|---|---|---|
| Commingled/Co-Spun | 0.38 g/m2 | 34 |
| Commingled/Co-Spun | 0.53 g/m2 | 37 |
| Commingled/Co-Spun | 0.76 g/m2 | 36 |
| Commingled/Co-Spun | 0.95 g/m2 | 34 |
| Commingled/Co-Spun | 1.37 g/m2 | 33 |
| Commingled/Co-Spun | 1.71 g/m2 | 35 |

**Derived from the Kirsch-Fuch equation

Example 13A

**[0619]** Media samples were prepared according to Method 9 and included a layer of large fine fibers (having a basis weight of at least 0.54 g/m$^2$) underneath a layer of mixed 0.5 μm fibers and 1.4 μm fibers.

**[0620]** SEM imaging provided a visual confirmation of the ability to control media morphology (FIG. **14**A, FIG. **14**B). FIG. **14**A shows media including small fine fibers only (FIG. **14**A, panel A), media including layered fibers of mixed diameters (FIG. **14**A, panels B, E, J), or media including large fine fibers only (FIG. **14**A, panel M). FIG. **14**B shows media including small fine fibers only (FIG. **14**B, panel A), media including commingled fibers of mixed diameters (FIG. **14**B, panels D, I, L), or media including large fine fibers only (FIG. **14**B, panel M). The letters in each panel indicate the electrospinning sequence described in Table 1C.

**[0621]** Composite maximum pore size, mean flow pore size, and minimum pore size for each sample were measured by capillary flow porometry. Results are shown in Table 8A. A comparison of pore sizes for commingled mixed diameter fine fiber structures and layered mixed diameter fine fiber structures are shown in FIG. **14**C.

**[0622]** As seen in Example 8, the introduction of commingled large fine fibers within the network of small fine fibers increased pore sizes relative to layers including small fine fibers alone, despite the higher basis weight observed for those layers (see Table 8A & FIG. **14**C).

**[0623]** Results of the evaluation of air filtration performance via HEFS bench testing are shown in Table 8B. Figure of Merit (FOM) values are shown in Table 8B and FIG. **14**D. Pressure drop (dP) values are shown in Table 8B and in FIG. **14**E (Set A, Set B, Set E, Set J, and Set M of Table 1C) and FIG. **14**F (Set A, Set D, Set I, Set L, and Set M of Table 1C); in FIG. **14**E and FIG. **14**F, the plots also show values for comparative liquid media products including fine glass fibers having a rating of 1,000 for particles <4 μm or having a β rating of 1,000 for particles <5 μm. Efficiency values (over-all β ratings) are shown in FIG. **14**G (Set A, Set B, Set E, Set J, and Set M of Table 1C) and FIG. **14**H (Set A, Set D, Set I, Set L, and Set M of Table 1C); the plots also show values for comparative liquid media products including fine glass fibers having a β rating of 1,000 for particles <4 μm or having a β rating of 1,000 for particles <5 μm.

**[0624]** These results show that at comparable pressure drop values (for example, 2-3 mm $H_2O$) through the various structures, a layered configuration with 38% large fiber content exhibited the highest efficiency and best FOM. Moreover, comparison of similar structures with other small and large fiber diameter combinations as discussed above (for example, 0.25 μm/1 μm and 0.25 μm/1.4 μm) show that the combination 0.5 μm/1.4 μm-diameter fibers does not yield the optimum media filtration performance (lower efficiencies and higher pressure drop).

Example 13B

**[0625]** Media samples were prepared according to Method 11 and included a layer of large fine fibers (having a basis weight of at least 0.54 g/m$^2$) underneath a layer of commingled 0.5 μm fibers and 1.4 μm fibers.

**[0626]** The resulting commingled fine fiber layer had a basis weight of 0.84 g/m$^2$, 1.25 g/m$^2$, 1.67 g/m$^2$, or 2.09 g/m$^2$ (for precursor solutions delivered for 2 minutes, 3 minutes, 4 minutes, or 5 minutes, respectively). The commingled fine fiber layer included 17% large fiber (1.4 μm diameter) content on fiber count basis.

**[0627]** Results of the evaluation of air filtration performance via HEFS bench testing are shown in Table 8C and FIG. **14**I. These results demonstate that with commingled structures of 0.5 μm and 1.4 μm fibers, the FOM can suffer because of a drastic increase in pressure drop (dP) without commensurate improvement in efficiency. For example, increasing the basis weight from 0.84 g/m$^2$ to 2.09 g/m$^2$ reduces the penetration by approximately half (39.9 to 22.22) but at almost doubles the dP (4.4 to 8 mm $H_2O$).

TABLE 8A

Summary of pore size measurements via capillary flow porometry

| | Max Pore Size (μm) | Mean Flow Pore Size (μm) | Min Pore Size (μm) |
|---|---|---|---|
| Cerex alone (bare scrim) | 65.1 ± 15.6 | 48.5 ± 10.0 | 23.6 ± 11.7 |
| Set A-100% Small Fine Fibers | 7.0 ± 4.7 | 2.8 ± 0.3 | 2.5 ± 0.3 |
| Set B-6% Large Fine Fibers, Layered | 11.3 ± 3.0 | 3.5 ± 0.3 | 3.2 ± 0.3 |

TABLE 8A-continued

Summary of pore size measurements via capillary flow porometry

| | Max Pore Size (μm) | Mean Flow Pore Size (μm) | Min Pore Size (μm) |
|---|---|---|---|
| Set E-17% Large Fine Fibers, Layered | 6.1 ± 1.4 | 3.7 ± 0.4 | 3.3 ± 0.3 |
| Set J-38% Large Fine Fibers, Layered | 9.0 ± 1.4 | 5.6 ± 1.0 | 5.0 ± 0.7 |
| Set D-6% Large Fine Fibers, Commingled | 9.3 ± 1.9 | 4.4 ± 0.3 | 3.6 ± 0.5 |
| Set I-17% Large Fine Fibers, Commingled | 9.0 ± 1.0 | 4.4 ± 0.8 | 3.5 ± 0.8 |
| Set L-38% Large Fine Fibers, Commingled | 15.1 ± 2.2 | 8.1 ± 0.4 | 6.6 ± 0.5 |
| Set M-100% Large Fine Fibers | 16.5 ± 7.1 | 8.1 ± 2.3 | 6.2 ± 1.1 |

TABLE 8B

Summary of FOM values as measured from HEFS

| | % Penetration | dP (mm $H_2O$) | FOM |
|---|---|---|---|
| Cerex alone (bare scrim) | 98.7 | 0.7 | 14 |
| Set A-100% Small Fine Fibers | 53 | 2.8 | 166.8256 |
| Set B-6% Large Fine Fibers, Layered | 59.7 | 2.4 | 158.1367 |

TABLE 8B-continued

Summary of FOM values as measured from HEFS

| | % Penetration | dP (mm $H_2O$) | FOM |
|---|---|---|---|
| Set E-17% Large Fine Fibers, Layered | 58.7 | 2.3 | 170.4159 |
| Set J-38% Large Fine Fibers, Layered | 44 | 3 | 201.3455 |
| Set D-6% Large Fine Fibers, Commingled | 61.3 | 2.6 | 137.5523 |
| Set I-17% Large Fine Fibers, Commingled | 55.9 | 3 | 141.6751 |
| Set L-38% Large Fine Fibers, Commingled | 63.5 | 2.5 | 135.4566 |
| Set M-100% Large Fine Fibers | 71.5 | 2 | 122.5782 |

TABLE 8C

Summary of FOM values as measured from HEFS

| | % Penetration | dP (mm H2O) | FOM |
|---|---|---|---|
| Commingled-0.84 g/$m^2$ | 39.9 | 4.4 | 153.637 |
| Commingled-1.25 g/$m^2$ | 38.2 | 5 | 143.5212 |
| Commingled-1.67 g/$m^2$ | 30.7 | 5.8 | 148.79 |
| Commingled-2.09 g/$m^2$ | 22.2 | 8 | 139.3554 |

TABLE 9

Comparison of initial pressure drop (dP) and over-all efficiencies (β values) for 3 μm particles (benchmarked against a glass fiber-containing media with β = 1000 for <4 μm particles)

| | Method | Clean Media dP (psi) | % Improvement in dP* | Over-all β (3 μm) | % Improvement in over-all β* |
|---|---|---|---|---|---|
| Glass (β = 1000 for <4 um) | n/a | 5.72 | — | 696 | — |
| 0.25 μm Small and 1 μm Large Fibers | | | | | |
| Supported Co-Spun 1.9 g/$m^2$ 10% Large | Method 7 | 1.79 | 69 | 239 | (−66) |
| L/S/Commingled/L-2% Large | Method 6, Table 1A, Set A6 | 3.07 | 46 | 487 | (−30) |
| Supported Layered-5% Large | Method 4, Table 1A, Set B | 0.84 | 85 | 65 | (−91) |
| Supported-100% Small 1 g/$m^2$ | Method 4, Table 1A, Set A | 3.63 | 37 | 916 | 32 |
| 0.5 μm Small and 1.4 μm Large Fibers | | | | | |
| Supported 100% Small | Method 9, Table 1C, Set A | 0.93 | 84 | 108 | (−84) |
| 0.25 μm Small and 1.4 μm Large Fibers | | | | | |
| Supported Co-Spun 1.71 g/$m^2$ 6.5% Large | Method 10 | 2.67 | 53 | 1358 | 95 |
| L/S/Commingled/L-100% Small | Method 12, Table 1B, Set A | 3.11 | 46 | 2607 | 275 |
| L/S/Commingled/L-17% Large | Method 12, Table 1B, Set L | 2.36 | 59 | 602 | (−14) |
| Supported Layered-1% Large | Method 8, Table 1B, Set A5 | 1.11 | 81 | 205 | (−71) |
| L/S/S/S/L | Method 13 | 3.76 | 34 | 6685 | 860 |

*% Improvement is reported against glass fiber-containing media (nominal $\beta_{<4\ um}$ = 1,000) as [|(Sample value − Glass value)|/Glass value] × 100%; negative signs and parentheses are added to indicate worse performance

Example 14

**[0628]** This Example describes the comparison of the best performing (in terms of pressure drop and efficiency for 3 μm particles) samples from three sets of media incorporating small (0.25 μm or 0.5 μm diameter) and large (1 μm or 1.4 μm diameter) fibers. Combinations of fiber diameters included: 0.25 μm and 1 μm; 0.5 μm and 1.4 μm; and 0.25 μm and 1.4 μm.

**[0629]** The results are summarized in Table 9. Percent improvement in initial pressure drop (dP) and over-all efficiencies (β values) for 3 μm particles (benchmarked against a glass fiber-containing media with β=1000 for <4 μm particles) are shown in FIG. **15**A. As shown in FIG. **15**A, four structures exhibited significant improvements in both over-all efficiency and dP compared to the glass fiber-containing media. In this plot, Quadrant I is the target zone (i.e., benefits in both dP and β compared to the glass fiber-containing media). Notably, none of the mixed fiber diameter media structures fell into Quadrant III (declines in both dP and β compared to the glass fiber-containing media). As shown in FIG. **15**B, all of the mixed fiber diameter media structures show comparable or better pressure drop than a glass containing media structure (with β=1000) for various particles sizes.

**[0630]** Because the mixed fiber diameter media structures can be produced using a wide processing window, a desired efficiency may be targeted.

Example 15

**[0631]** A sample prepared according to Method 12 (L/S/Table 1B, Set M/L) was analyzing according to the "Fine Fiber Layer Thickness" method. An exemplary image is shown in FIG. **16**A, wherein the full depth of the fine fiber layer is visible in cross-section, and fibers of the support layer are partially visible at the bottom of the image.

**[0632]** FIG. **16**B shows delineation of the fine fiber cross-section using a polygon tool. FIG. **16**C shows the image after the area outside the selected fine fiber cross-section as been cleared. FIG. **16**D shows the area of the selected fine fiber cross-section after it was re-colored white using the threshold level tool (to compensate for fibers on the borders of the selected section), and the dashed line indicates the maximum thickness in the image that was measured is recorded (5.97 μm). Five of these maximum values were rounded to the nearest tenth of a micron and then these rounded values then averaged. Results are shown in Table 5.

**[0633]** The complete disclosure of all patents, patent applications, and publications, and electronically available material cited herein are incorporated by reference. In the event that any inconsistency exists between the disclosure of the present application and the disclosure(s) of any document incorporated herein by reference, the disclosure of the present application shall govern. The foregoing detailed description and examples have been given for clarity of understanding only. No unnecessary limitations are to be understood therefrom. The invention is not limited to the exact details shown and described, for variations obvious to one skilled in the art will be included within the invention defined by the claims.

**1**. A filtration media comprising:

a support layer; and

a fine fiber layer,

wherein the fine fiber layer is deposited on the support layer, and

wherein the fine fiber layer comprises large fine fibers and small fine fibers, the large fine fibers having an average diameter of at least 1 μm and are at least 3 times the average diameter of small fine fibers.

**2**. The filtration media of claim **1**, wherein the fine fiber layer comprises a first layer of fine fibers, and wherein the first layer of fine fibers comprises the large fine fibers and the small fine fibers.

**3**. The filtration media of claim **1**, wherein the fine fiber layer comprises a first layer of fine fibers and a second layer of fine fibers, wherein the first layer of fine fibers is deposited on the support layer, and the second layer of fine fibers is deposited on the first layer of fine fibers.

**4**. The filtration media of claim **3**, wherein the first layer of fine fibers comprises fibers having an average diameter at least 3 times the average fiber diameter of a fine fiber of the second layer of fine fibers.

**5**. The filtration media of claim **3**, wherein the second layer of fine fibers comprises fibers of two different diameters,

wherein the fine fibers of two different diameters comprise small fine fibers and large fine fibers, the large fine fibers having an average diameter at least 3 times the average diameter of the small fine fibers, and

wherein the small fine fibers are deposited on the first layer of fine fibers and the large fine fibers are deposited on the small fine fibers.

**6**. The filtration media of claim **3**, wherein the second layer of fine fibers comprises fibers of two different diameters,

wherein the fine fibers of two different diameters comprise small fine fibers and large fine fibers, the large fine fibers having an average diameter at least 3 times the average diameter of the small fine fibers, and

wherein the small fine fibers are commingled with the large fine fibers.

**7**. The filtration media of claim **1**, wherein at least some of the fine fibers are prepared by a method comprising:

providing a fiber-forming polymer;

providing a polymer-reactive resinous aldehyde composition, wherein the polymer-reactive resinous aldehyde composition is reactive with the fiber-forming polymer; and

combining the fiber-forming polymer and reactive resinous aldehyde composition to form a plurality of fine fibers.

**8**. The filtration media of claim **1**, wherein at least some of the fine fibers are prepared by a method comprising:

providing a fiber-forming polymer, wherein the fiber-forming polymer comprises a nonreactive polymer, that is a polymer unable to crosslink with the polymer-non-reactive resinous aldehyde composition;

providing a polymer-non-reactive resinous aldehyde composition, wherein the polymer-non-reactive resinous aldehyde composition comprises one or more reactive groups that are capable of self-crosslinking; and

combining the fiber-forming polymer and reactive resinous aldehyde composition to form a plurality of fine fibers.

**9**. The filtration media of claim **1**, wherein at least some of the fine fibers are prepared by a method comprising:

providing at least one fiber-forming polymer;

providing at least two reactive additives reactive with each other, and optionally reactive with the fiber-forming polymer; and

combining the at least one fiber-forming polymer and the at least two reactive additives under conditions effective to form a plurality of fine fibers.

**10**. The filtration media of claim **1**, wherein the support layer comprises a spunbond layer.

**11**. The filtration media of claim **1**, wherein the large fine fibers have a diameter at least 0.2 μm greater than a diameter of the small fine fibers.

**12**. The filtration media of claim **1**, wherein the support layer and the fine fiber layer form a composite having a composite mean flow pore size, and wherein the composite mean flow pore size is up to 11 μm.

**13**. The filtration media of claim **1**, wherein the fine fiber layer has a thickness of up to 50 μm.

**14**. The filtration media of claim **1**

wherein the small fine fibers have an average diameter of at least 0.2 μm; or

wherein the small fine fibers have an average diameter of up to 0.6 μm;

or both.

**15**. The filtration media of claim **1** wherein the fine fibers are compatible with at least one of a hydraulic fluid, fuel, or lubricant.

**16**. A filter element comprising the filtration media of claim **1**.

**17**. The filter element of claim **16**, wherein the filter element comprises an efficiency layer, and the efficiency layer comprises the filtration media.

**18**. The filter element of claim **17**, wherein the filter element further comprises a loading layer.

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