Hansen Solubility Parameters

F. Ruttens

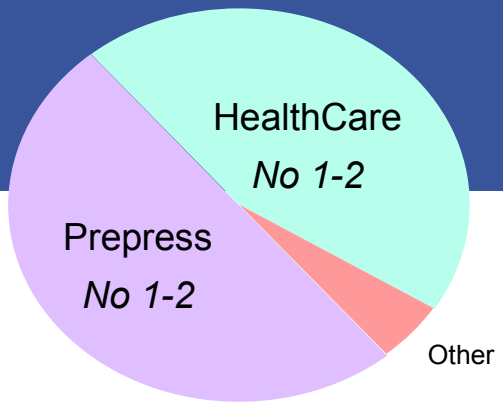
Efficient and faster time-to-market

Open Innovation Platform for
Materials & Coating Research

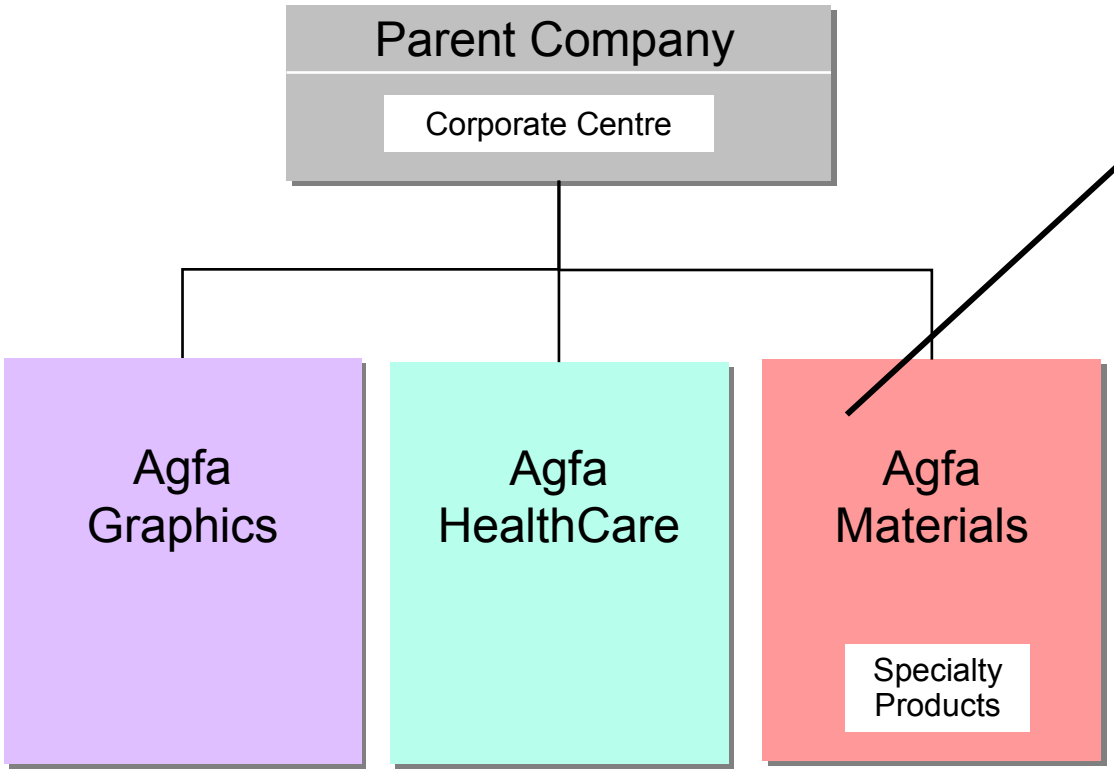
Extend your Reach

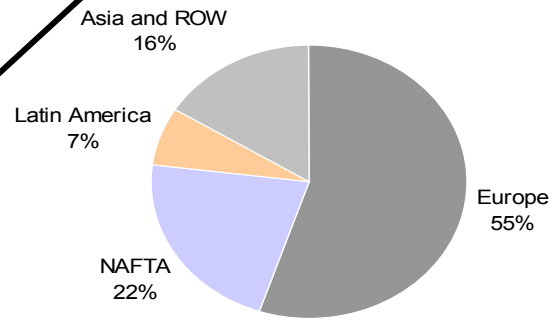
Advanced Chemical and Physical Analytics
Joint Development Projects

Agfa-Gevaert Group

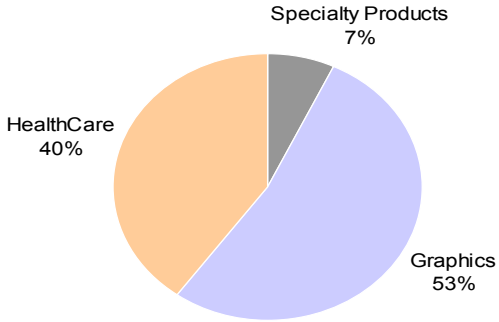


Agfa-Gevaert Group



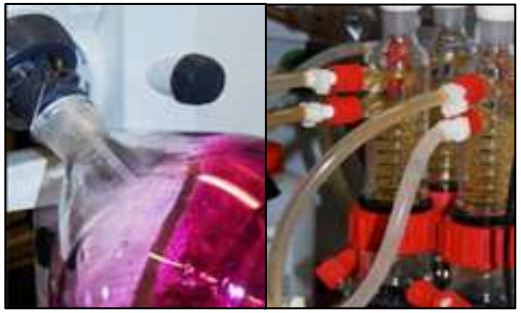


Sales by region



Sales per business group

Agfa's Materials Technology Centre



Molecular Ingredients

- Sourcing, design and synthesis
  - Functional polymers
  - Dispersants
  - Dyes
  - Pigments
  - Functional ingredients
- Structure – activity relation

Formulations & dispersions

- Formulation discovery
- Structure – activity relation
- Dispersion technology
- Process scale-up
- Pilot Lab

Reaction calorimetry

Security

REACH

Analytical competences

- Organic and Inorganic Analysis
- Colloids, Surfaces and Particles
- Thermal Analysis
- Microscopy and Material Optics
- High Throughput Techniques & Mechanical Testing
- Climate Testing and Weathering

Agfa's Advanced Analytical Services

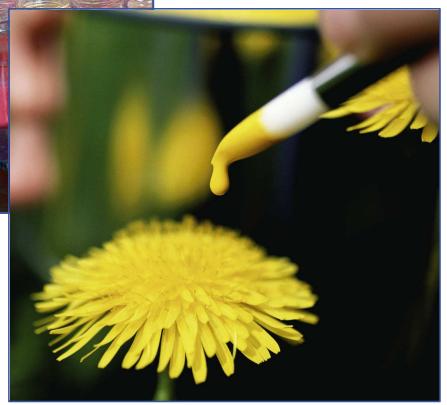
Agfa's Advanced Analytical Services

Trouble shooting and Failure Analysis

Contaminant Identification

Materials Analysis and Testing

High Throughput Analytics



Deformulation

Agfa-Labs' toolbox

High Throughput Formulation

Hansen Solubility Parameters

High Throughput Analysis

Miscellanea

Hansen Solubility Theory

Hildebrand solubility parameter δ

- Based on the principle :
  - Like seeks like
  - Like dissolves like
  - Similia similibus solvuntur

Cohesive energy density

Energy of evaporation

$$\delta^2 = \left(\frac{E}{V_m}\right) = \left(\frac{\Delta H_{evap} - R.T}{V_m}\right)$$

Molar volume

Hansen Solubility Parameters

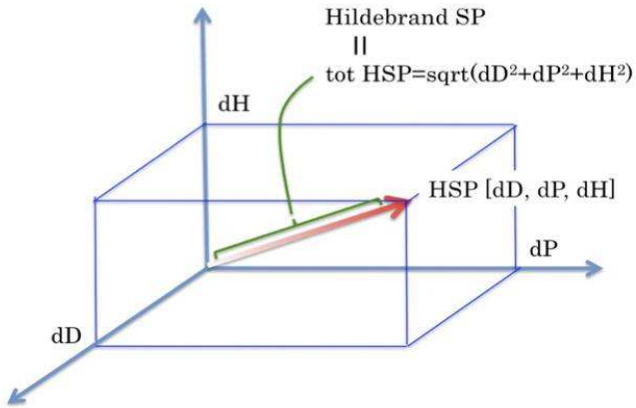
- The total cohesive energy can be divided in 3 components
  - (atomic) dispersion forces (VanderWaals…)
  - (molecular) permanent dipole-permanent dipole forces
  - (molecular) hydrogen bonding (electron exchange)

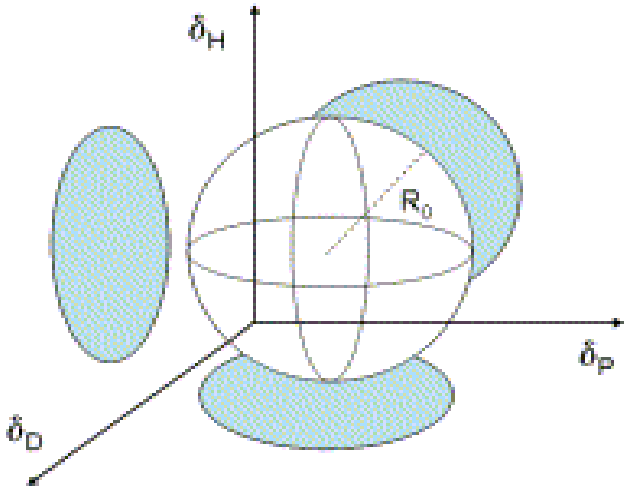
$$\delta^2 = \delta_D{}^2 + \delta_P{}^2 + \delta_H{}^2$$

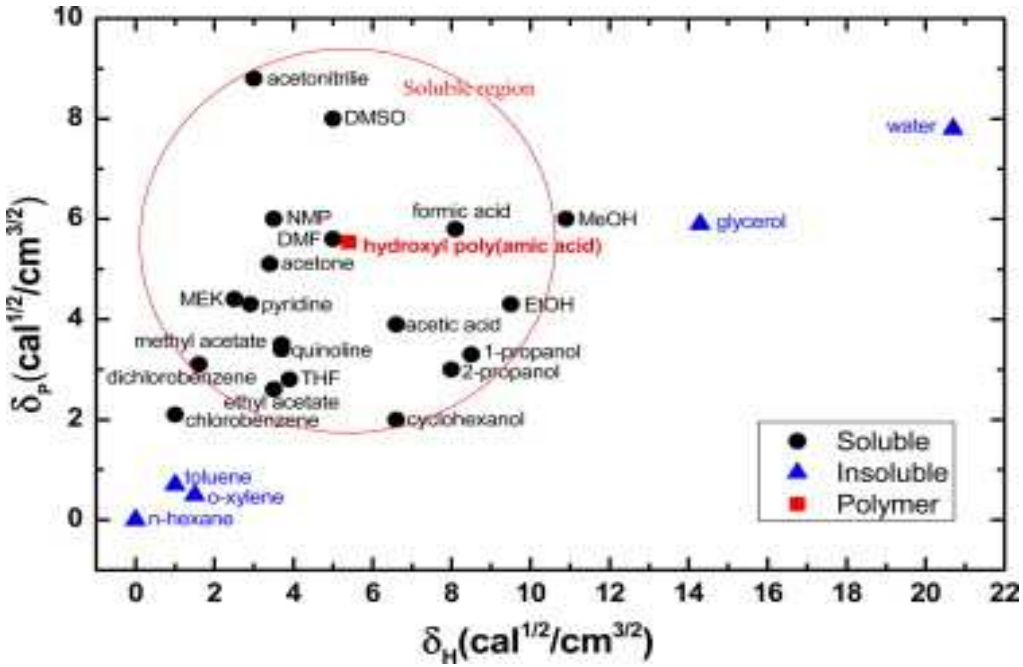
Each solvent, polymer, pigment…
can be described by a set of
(δD, δP, δH) coordinates

Hansen solubility parameters

- 3D representation
  - cartesian space coordinates (δD, δP, δH)
  - Sphere of solubility

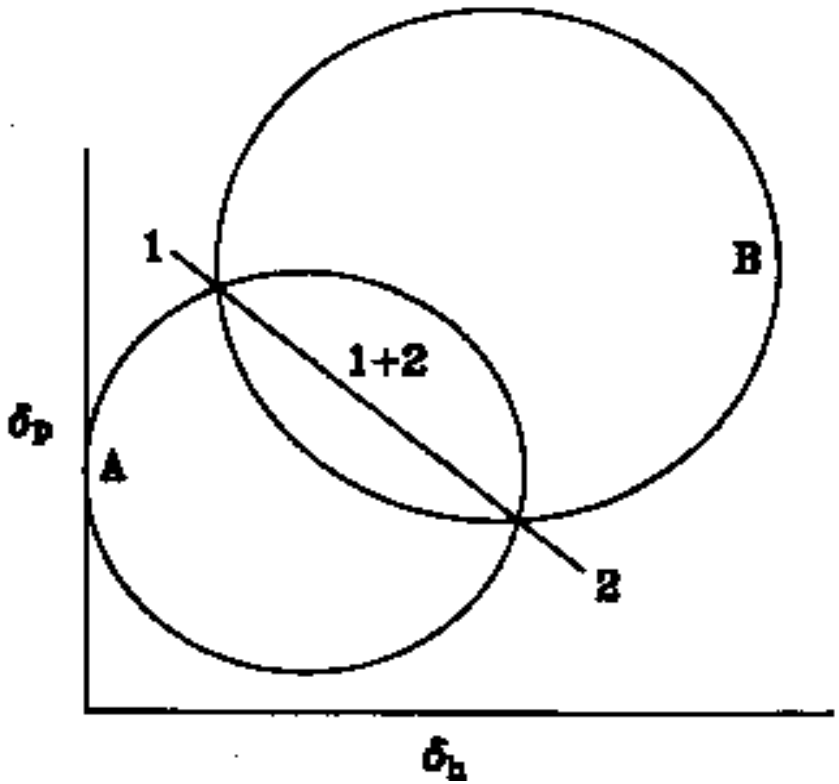






Hansen solubility parameters

- Solvent mixtures
  - Two non-solvents can be mixed to a good solvent
  - Two immiscible polymers can be brought to an homogeneous solution

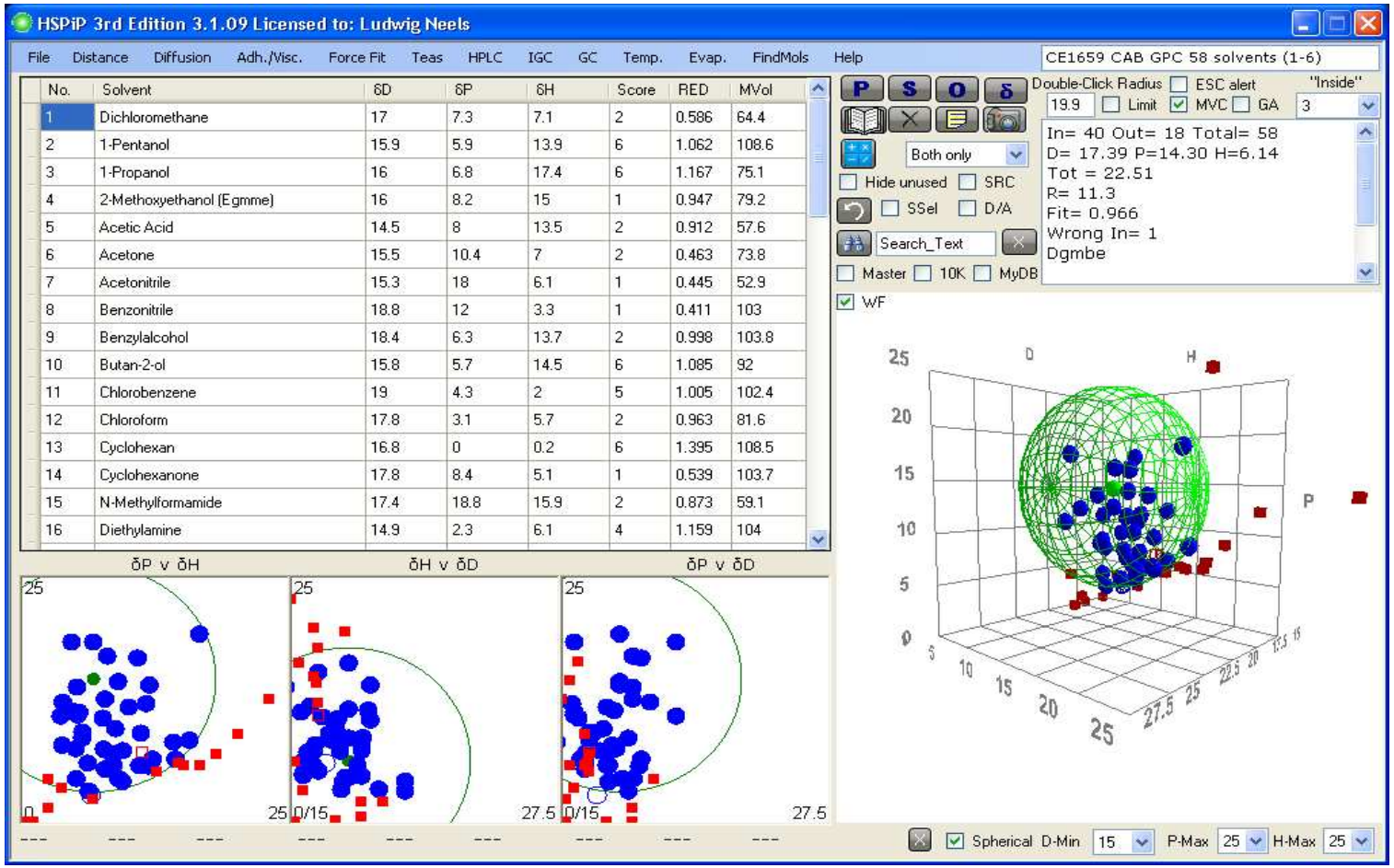


A,B : Polymers

1,2 : solvents

Hansen solubility parameters

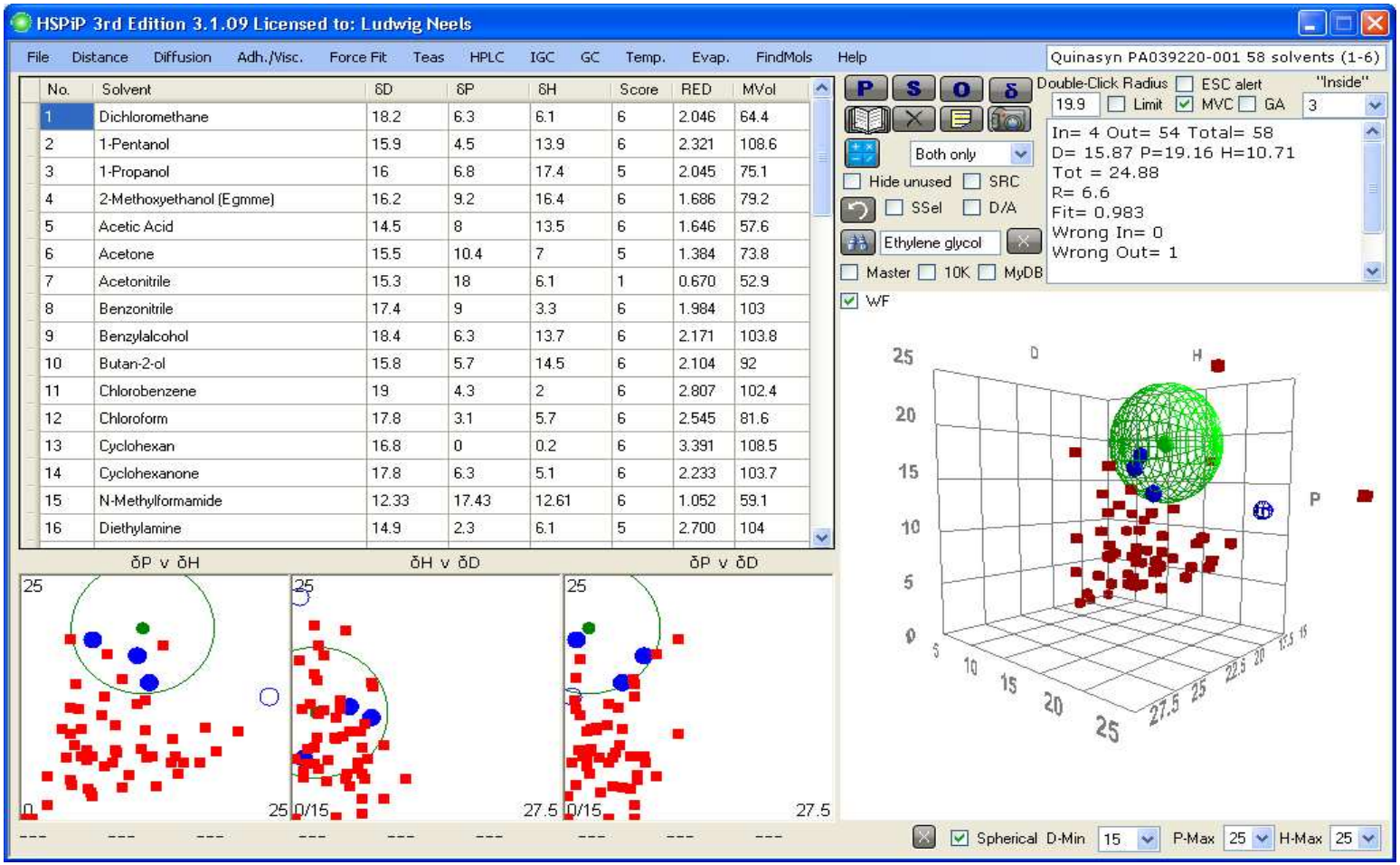
- Solubility sphere of a polymer : CAB



No.	Solvent	δD	δP	δH	Score	RED	MVol
1	Dichloromethane	17	7.3	7.1	2	0.586	64.4
2	1-Pentanol	15.9	5.9	13.9	6	1.062	108.6
3	1-Propanol	16	6.8	17.4	6	1.167	75.1
4	2-Methoxyethanol (Egmme)	16	8.2	15	1	0.947	79.2
5	Acetic Acid	14.5	8	13.5	2	0.912	57.6
6	Acetone	15.5	10.4	7	2	0.463	73.8
7	Acetonitrile	15.3	18	6.1	1	0.445	52.9
8	Benzonitrile	18.8	12	3.3	1	0.411	103
9	Benzylalcohol	18.4	6.3	13.7	2	0.998	103.8
10	Butan-2-ol	15.8	5.7	14.5	6	1.085	92
11	Chlorobenzene	19	4.3	2	5	1.005	102.4
12	Chloroform	17.8	3.1	5.7	2	0.963	81.6
13	Cyclohexan	16.8	0	0.2	6	1.395	108.5
14	Cyclohexanone	17.8	8.4	5.1	1	0.539	103.7
15	N-Methylformamide	17.4	18.8	15.9	2	0.873	59.1
16	Diethylamine	14.9	2.3	6.1	4	1.159	104

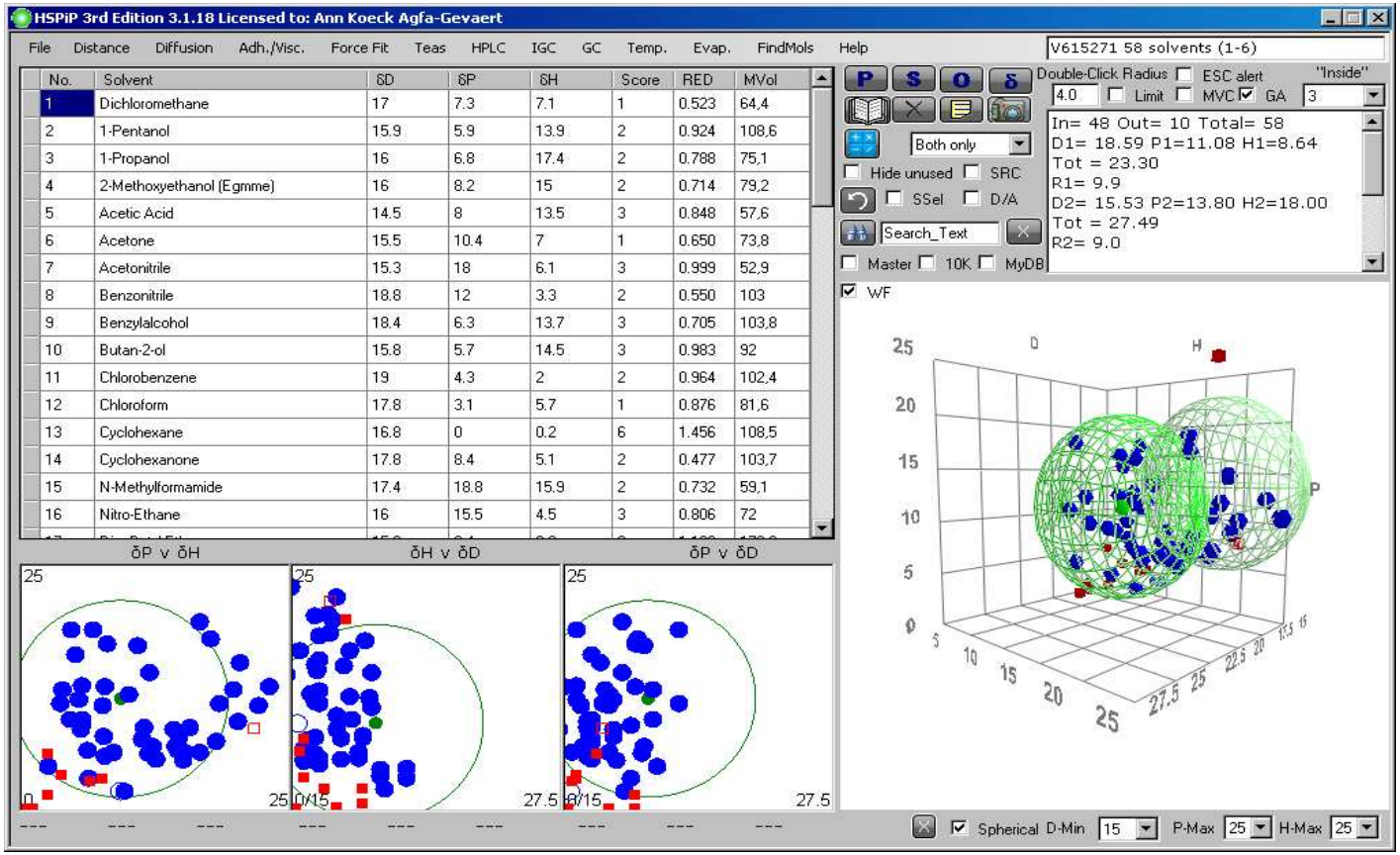
Hansen solubility parameters

- “Solubility” sphere of a pigment



Hansen solubility parameters

- Solubility sphereS for a dispersant
  - sphere 1 : dD = 18.59 / dP = 11.08 / dH = 8.64 (R = 9.9)
  - sphere 2 : dD = 15.53 / dP = 13.80 / dH = 18.00 (R = 9.0)



No.	Solvent	δD	δP	δH	Score	RED	MVol
1	Dichloromethane	17	7.3	7.1	1	0.523	64,4
2	1-Pentanol	15.9	5.9	13.9	2	0.924	108,6
3	1-Propanol	16	6.8	17.4	2	0.788	75,1
4	2-Methoxyethanol (Egmme)	16	8.2	15	2	0.714	79,2
5	Acetic Acid	14.5	8	13.5	3	0.848	57,6
6	Acetone	15.5	10.4	7	1	0.650	73,8
7	Acetonitrile	15.3	18	6.1	3	0.999	52,9
8	Benzonitrile	18.8	12	3.3	2	0.550	103
9	Benzylalcohol	18.4	6.3	13.7	3	0.705	103,8
10	Butan-2-ol	15.8	5.7	14.5	3	0.983	92
11	Chlorobenzene	19	4.3	2	2	0.964	102,4
12	Chloroform	17.8	3.1	5.7	1	0.876	81,6
13	Cyclohexane	16.8	0	0.2	6	1.456	108,5
14	Cyclohexanone	17.8	8.4	5.1	2	0.477	103,7
15	N-Methylformamide	17.4	18.8	15.9	2	0.732	59,1
16	Nitro-Ethane	16	15.5	4.5	3	0.806	72

Literature screening

524 references in CAS

HSP aid in coating technology

- when wet :
  - Dispersion stability (23 cit)
  - Thinners
  - Wetting of substrate
  - Solvent evaporation
  - Cross-linking
  - Skin formation
  - Stratification
  - Diffusion
- when dry :
  - Mechanical strength
  - Chemical resistance (15 cit)
  - Adhesion to substrate
  - Crazing
  - swelling
  - Gas permeability
  - Paint stripping

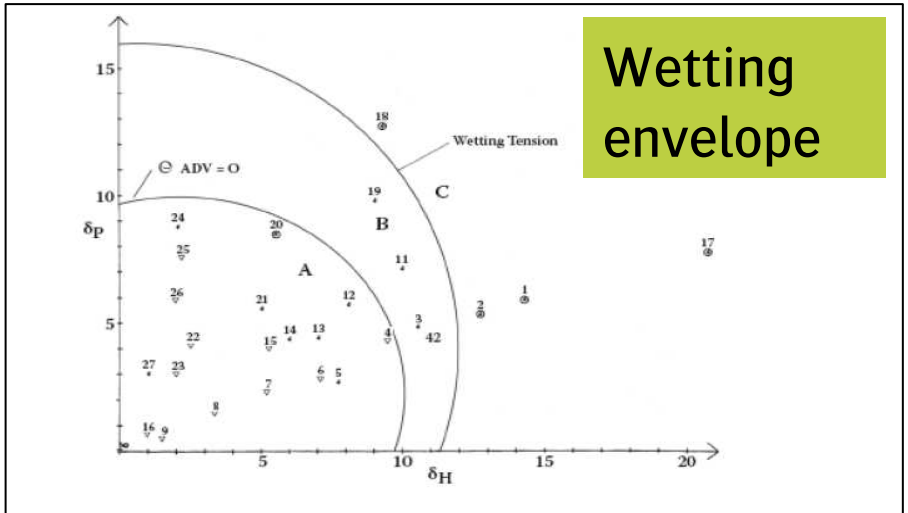
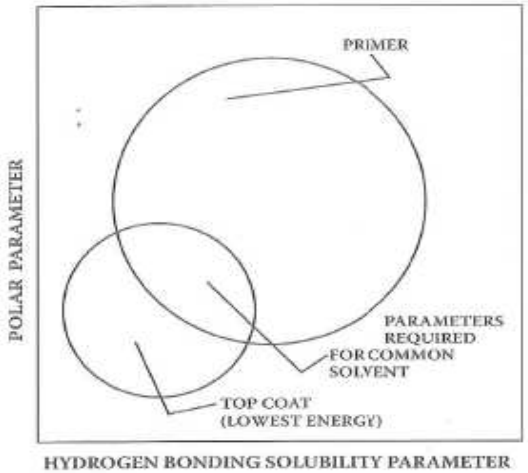
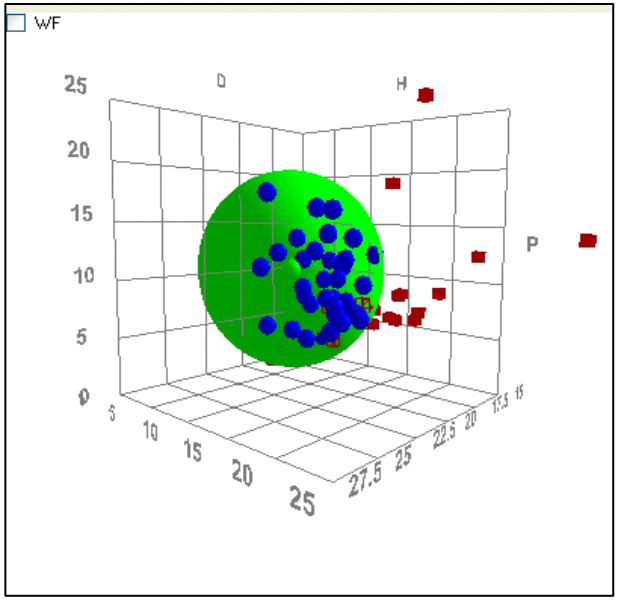


Fig.1. HSP surface characterization of an epoxy surface showing regions of spontaneous spreading of applied droplets (A), lack of dewetting of applied films (B), and dewetting of applied films (C). This characterization may not be valid for all epoxy surfaces. Units are $MPa^{1/2}$.

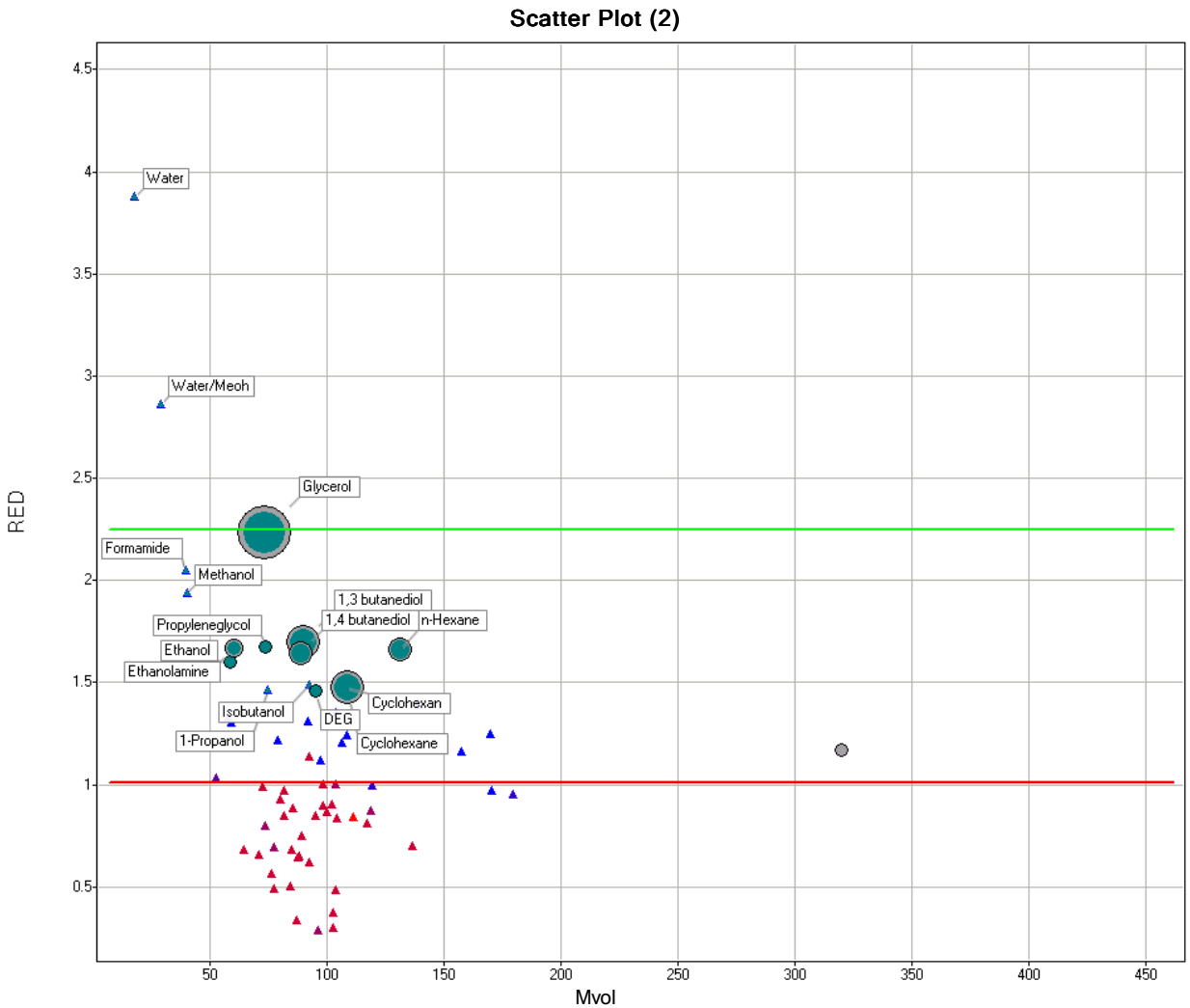
Self-stratifying coating system :



HSP aid in Environmental stress cracking and chemical resistance



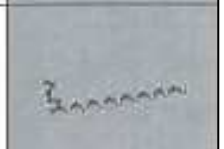
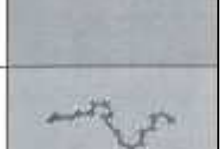
Hansen sphere for ABS



HSP aid in “green” Designer Solvents

- Cleaning of soils
- Safety and toxicity
- Biodegradable
- Ionic liquids
- Supercritical CO2
- Subcritical fluid extraction (food)
- Skin protection
- Toner print removal
- Fatty acid Me-esters (FAME’s)

Reference soil materials

Soil	#	$\delta_{Dispersion}$ MPa½	δ_{Polar} MPa½	$\delta_{Hydrogen\ Bonding}$ MPa½	Molecular Model Image
ASTM Fuel “A”	1	14.3	0	0	
Butyl Stearate	2	12.6	6.3	6.1	
Castor Oil[27]	3	13.6	6.0	10.5	
Ethyl Cinnamate	4	16.0	10.8	7.5	
Linseed Oil	5	13.5	3.5	3.7	
Tricresyl Phosphate	6	15.9	13.9	13.5	

HSP aid in nanotechnology

Controlled Morphology of Porous Polyvinyl Butyral Nanofibers

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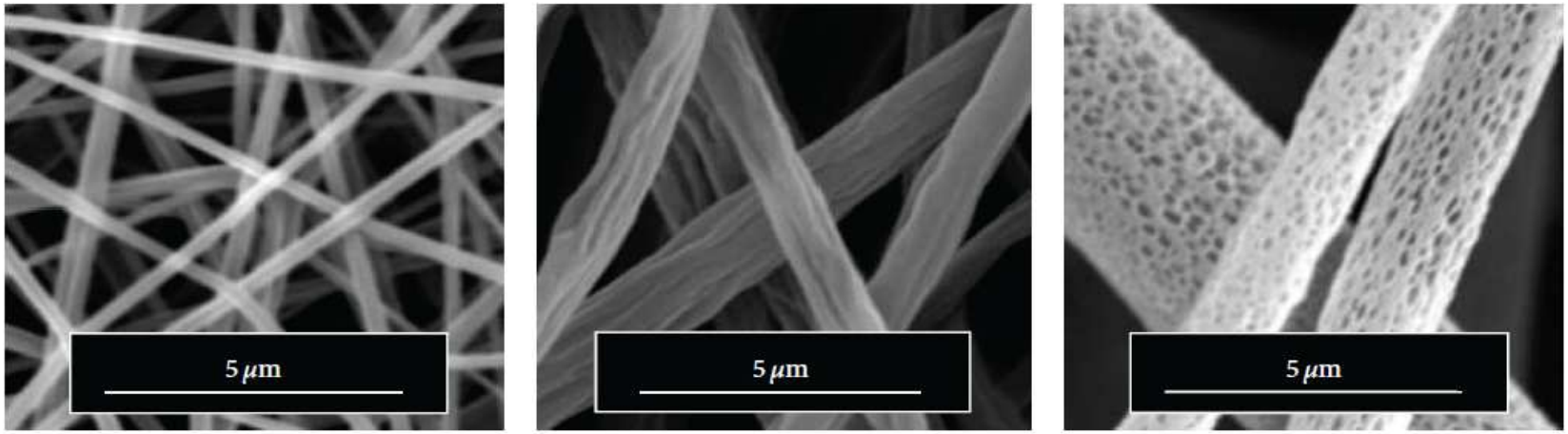
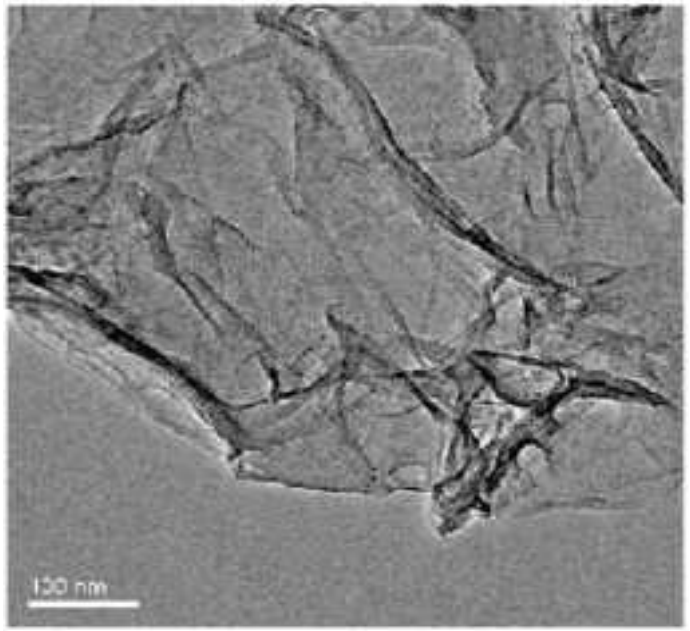
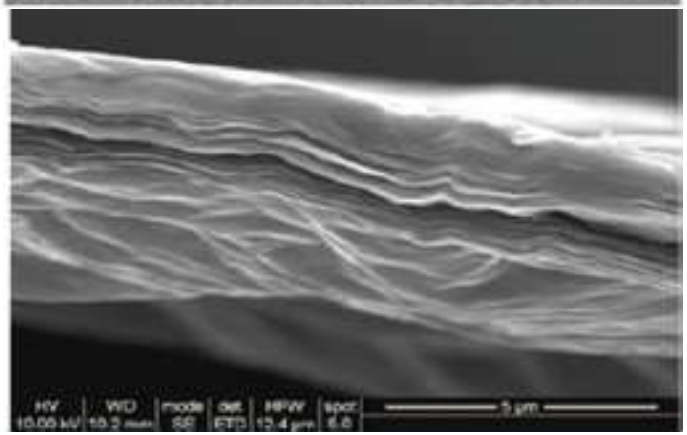


(a) (b) (c)

FIGURE 4: SEM images of PVB nanofibers prepared from 10 wt.% polymer solution from the mixtures: (a) ethanol/methanol (9/1 v/v), (b) ethanol/DMSO (9/1 v/v), (c) THF/DMSO (9/1 v/v).

HSP aid in nanotechnology





Colloidal Suspensions of Highly Reduced Graphene Oxide in a Wide Variety of Organic Solvents

Sungjin Park, Jinho An, Inhwa Jung, Richard D. Piner, Sung Jin An, Xuesong Li, Aruna Velamakanni, and Rodney S. Ruoff*

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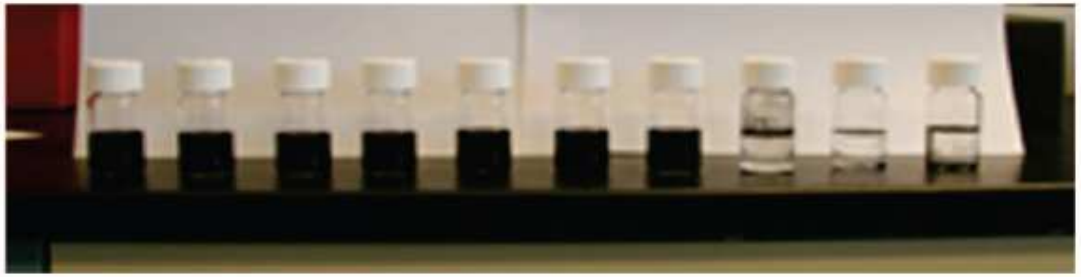
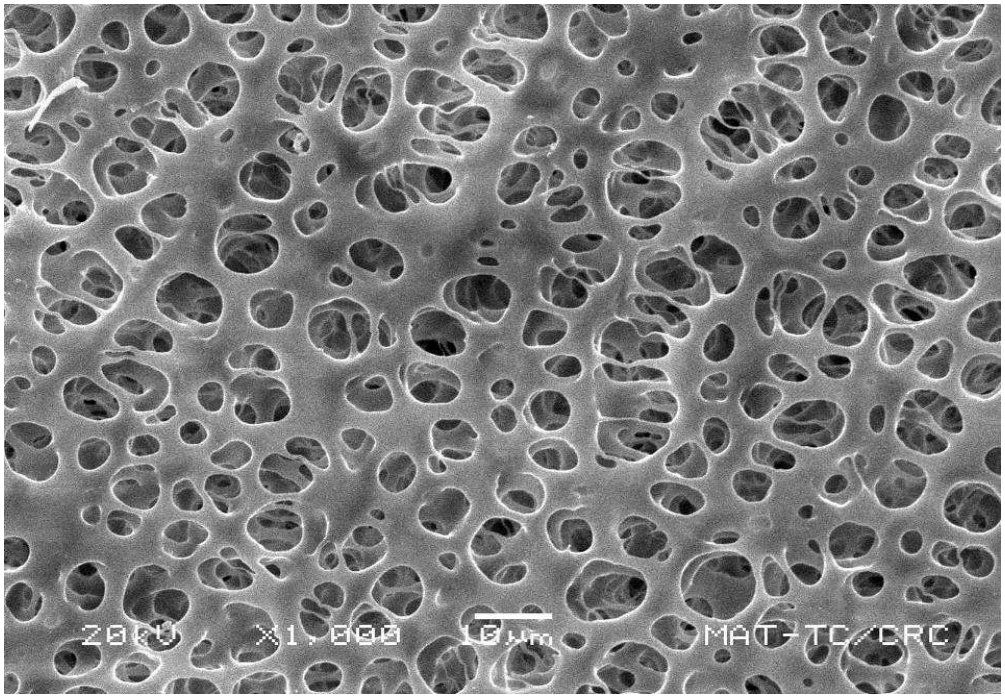


Colloidal suspensions of HRG sheets in various organic solvents, Volume ratio of added solvents:DMF:H_2O = 90:9:1, Added solvents from left: DMF, ethanol, acetone, THF, DMSO, NMP, acetonitrile, DCB, diethylether, and toluene

HSP aid in Barrier layers and Membranes

- Renewable barrier film design based on wood hydrolysate
- Gas separation
- Pervaporation membranes for separation of solvents (28 cit.)
- Permeability of membranes
- Phase diagrams
- Anti-biofouling
- Resist layers
- Pesticide
- Fire retardants
- Skin protection
- H-storage



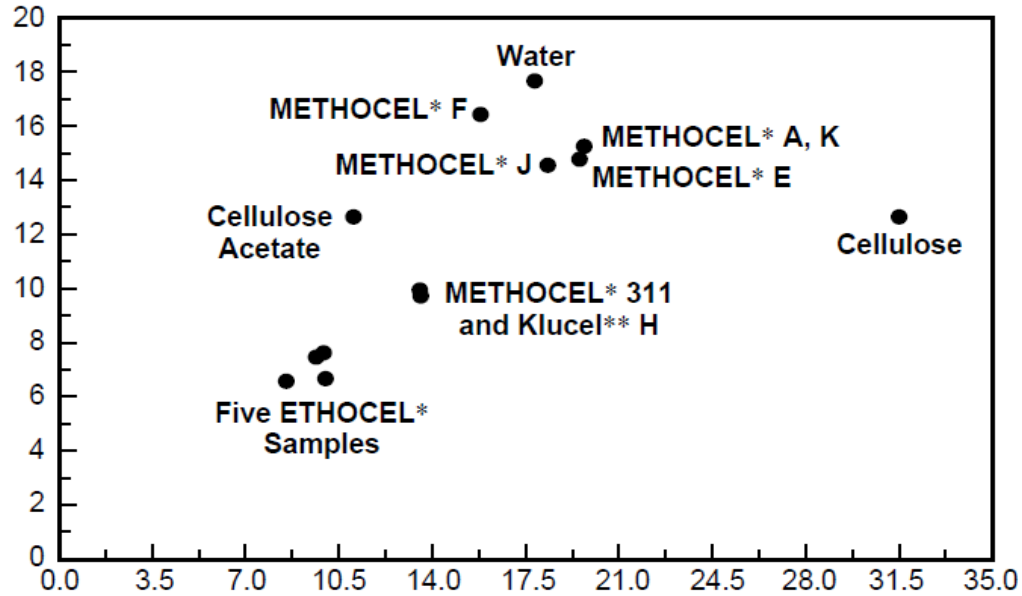
HSP aid in Pharmaceutical

- Controlled drug release
- Drug solubility in rats
- Hot melt extruded drug delivery
- Drug distribution in microspheres
- Co-crystallization
- Adsorption of cytotoxic drugs to nucle acids
- Nucleic acid hybridisation in polar, aprotic solvents
- Adsorption of proteins to polymers
- Bootstrap statistics
- Enzymology
- Extraction of bioactive components

DOW

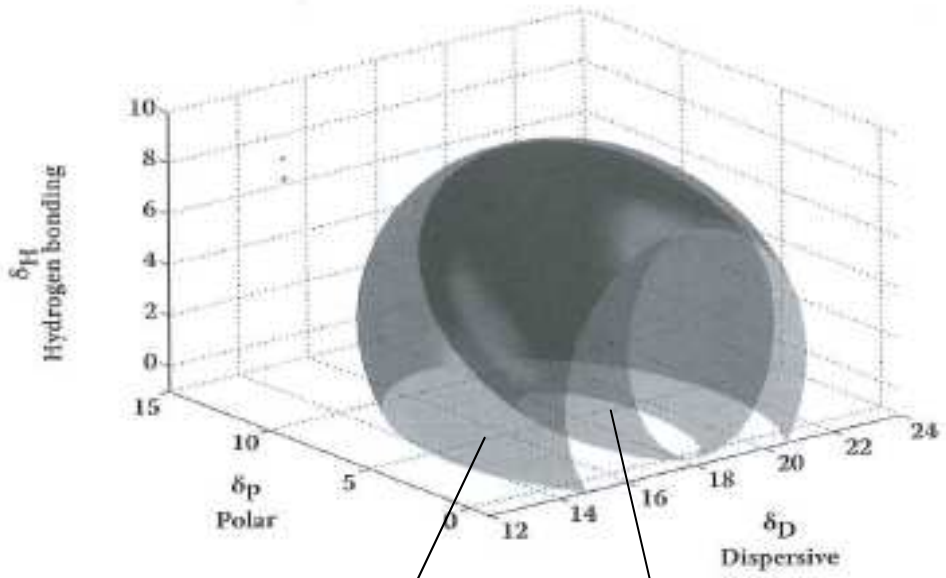
Hansen Solubility Parameters for Selected Cellulose Ether Derivatives and Their Use in the Pharmaceutical Industry

Figure 3 – Hansen Solubility Parameters for Cellulose Derivatives



HSP aid in Petrochemistry

- Asphaltene aggregation
- Bitumen
- Asphalt
- Crude oils
- Coal tar pit extraction
- Oil recovery
- Breaking heavy fuel
- Solute partition coefficients between polyolefins



Solubility sphere for light crude North Sea oil

Solubility sphere for heavy Venezuelan crude oil

HSP aid in Biological materials

- Cellulose
- Lignine
- Cholesterol
- Blood serum
- Fat
- DNA
- Skin
- Poly-L-lactine
- Hop
- Extraction bioactive components
- enzymology

Important source for biobased aromatic building blocks

SOLUBILITY PARAMETER PLOT FOR SKIN PERMEATION RATE

	δ_D	δ_P	δ_H	M_V	PERMEATION RATE
DMSO	18.4	16.4	10.2	71.3	● HIGH
DMF	17.4	16.7	11.3	77.0	
DMAC	16.8	11.5	10.2	92.5	
NMP	18.0	12.3	7.2	96.5	
MCL	18.2	6.3	6.1	63.9	O MODERATE
MEK	16.0	9.0	5.1	90.1	
ETH	15.8	8.8	19.4	58.5	
BAC	15.8	3.7	6.3	132.5	× LOW
PPC	20.0	18.0	4.1	85.0	
TOL	18.0	1.4	2.0	106.8	
BTA	19.0	16.6	7.4	76.8	
SUL	18.4	16.6	7.4	95.3	
OAC	15.8	2.9	5.1	196.0	✚ "0"

HSP in plastic processing

- Vulcanised NBR-rubber
- Composites with plasticizers
- Composite polymer blends
- Composites with fillers
- CAB, SBS, ABS, BR, CA, polyimide (19 cit)
- Precipitation polymerization (7 cit)
- Biopolymers
- Recycling plastics

And so many other applications…

HSP in Textiles

- Treating stained fabrics
- SFE surfactants on nylon
- Adsorption of colorants to fibers
- Whitening agents for cellulose

- HSP in Cosmetics
  - HSP of skin
  - Coloring of keratin fibres (hair)
  - Eye make-up removal
- HSP in Graphics
  - Ink Jet
  - Flexography
  - Paper industry
  - Adhesives for low SFE surfaces

- HSP in Electronics
  - Organic semiconductors
  - Alternative etching liquids for semi-conductors
  - Nano-lithography
  - Laminating resist layers
  - Conductive inks
- HSP in Energy
  - Liquifaction of PS in fuel
  - OPV (thiophene in acetophenone & mesitylene)
  - H-storage materials
  - Organic conductive coatings

HSP aid in Aromas and fragrances

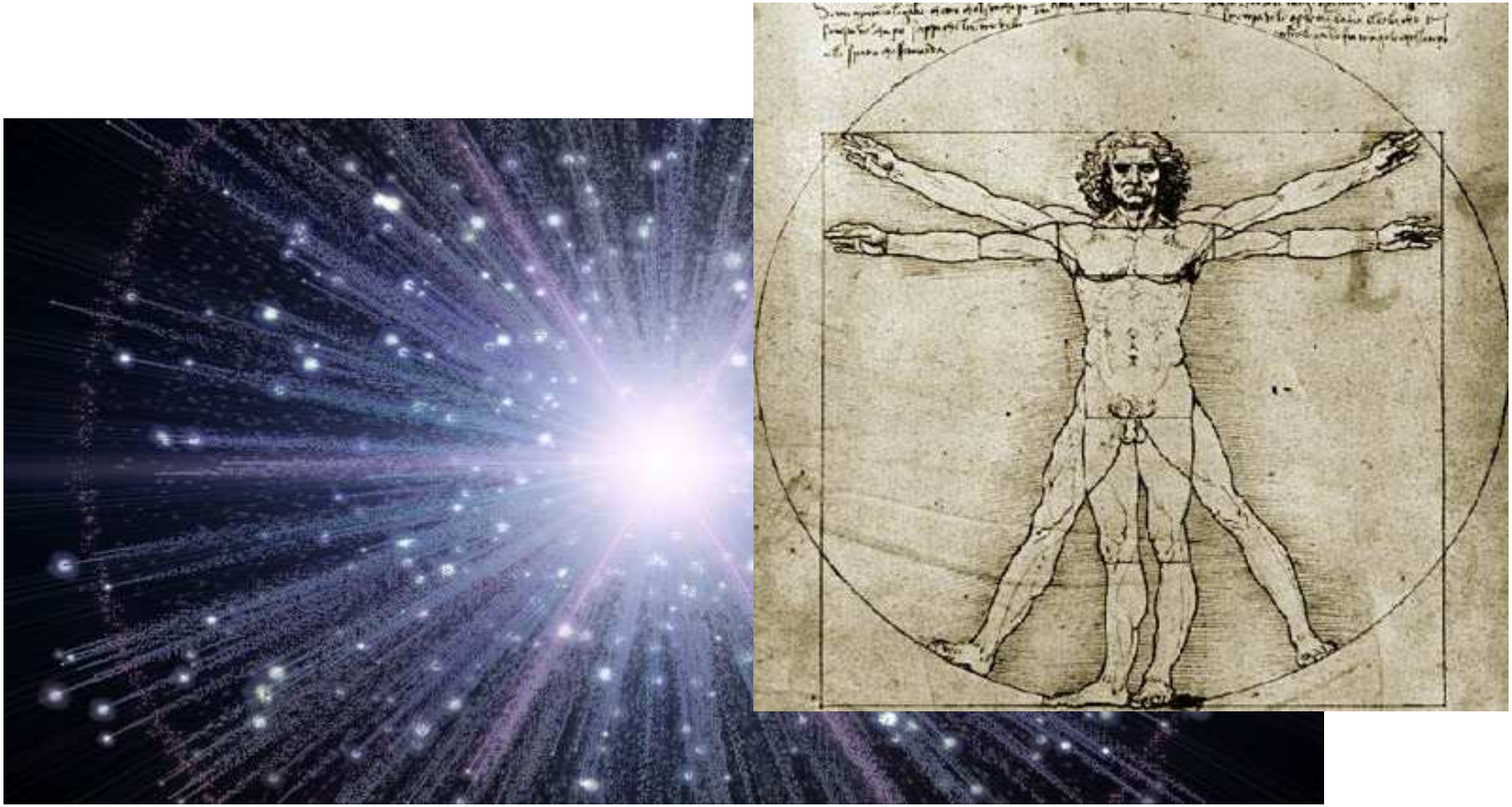
- Hiroshi Yamamoto

- HSP of natural herbs
- Offensive odor
- Hot and spicy
- Allergens for cosmetics

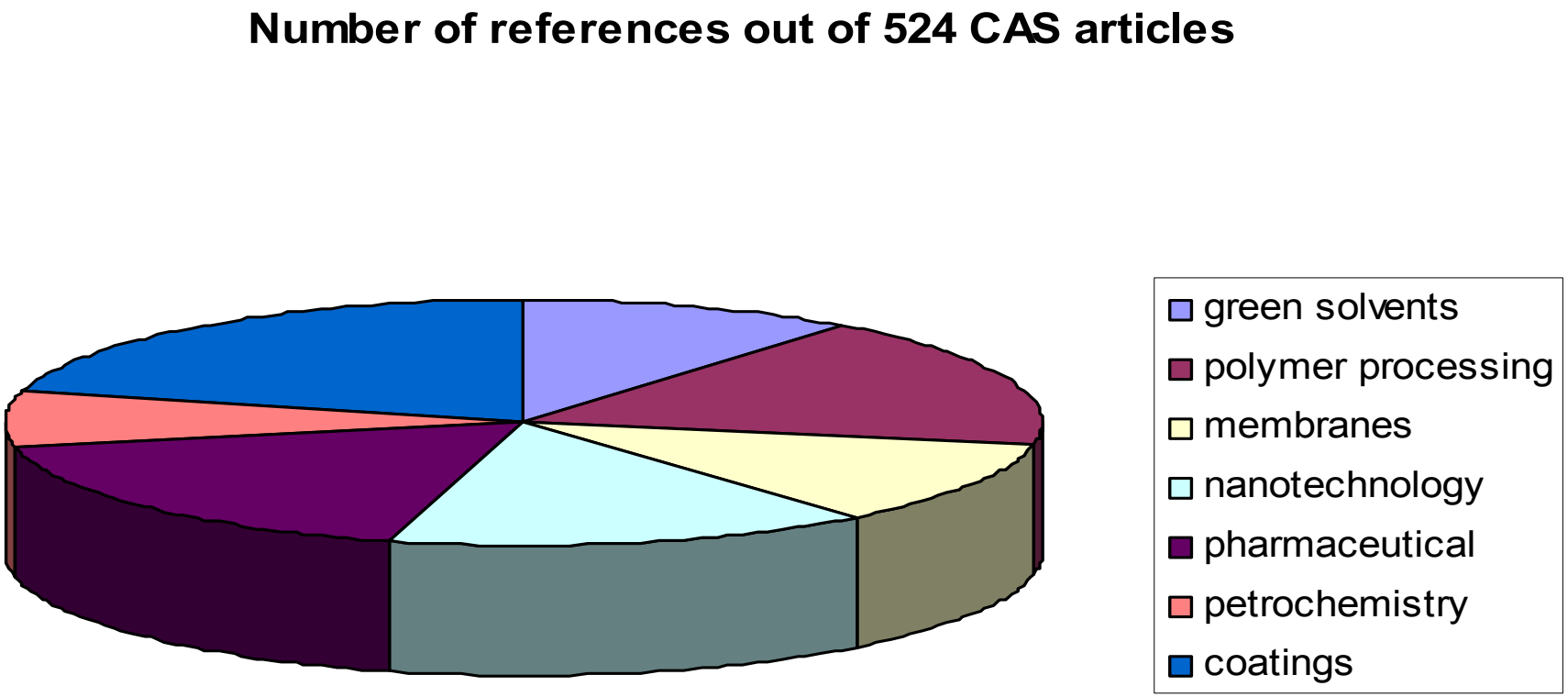
- 20 polymer sensored electronic nose
- Sensates in edible, oral, throat, skin, hair : menthanes = “fresh”
- Dispersion in air by aminoacids (aerosol)

Hansen solubility parameters

- The Grand Unification Theory?



Hansen solubility parameters



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