

Applications of nanospheres for water-based inks

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1. 세계 잉크 산업 개요
2. Water-based(w/b) inks 개요
3. RFE resins for w/b inks
4. Emulsion resins for w/b inks
5. HCC solurlyl resins & emulsions

Table 1. World-Printing Ink Production by Region 1998

Region	Volume (1000 tonnes)	Value (US\$ millions)	Annual Growth 1999-2000%
Americas	1,300	5,200	2-3
Asia-Pacific(a)	800	3,100	5-6
Europe (b)	1,100	4,200	1-2
Total	3,200	12,500	2-4

Note : (a) Includes production from the Middle East

(b) Includes production from Africa

Source: MTI from Industry Associations

Table 2. World-Leading Printing Ink Producing countries 1998

Rank	Country	Volume (1000 tonnes)	Value (US\$ millions)
1	USA	1,100	4,200
2	Japan	425	–
3	Germany	400	1,300
4	UK	150	680
5	China	100	400
6	France	92	470
7	India	85	300
8	Italy	80	350
9	Netherlands	75	300
10	South Korea	70	280

Source: MTI from Industry Associations

Chart 1. World-Printing Ink Market by Ink Type 1998

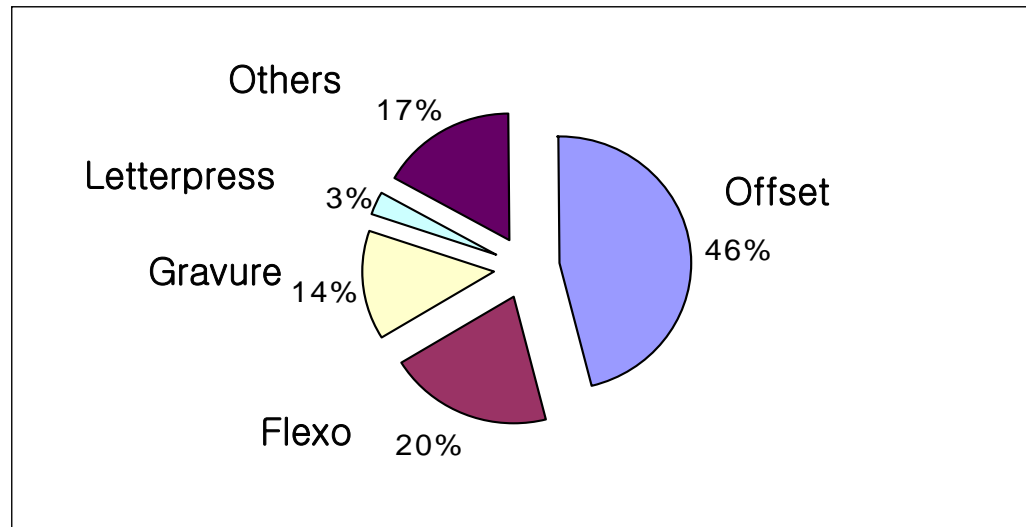
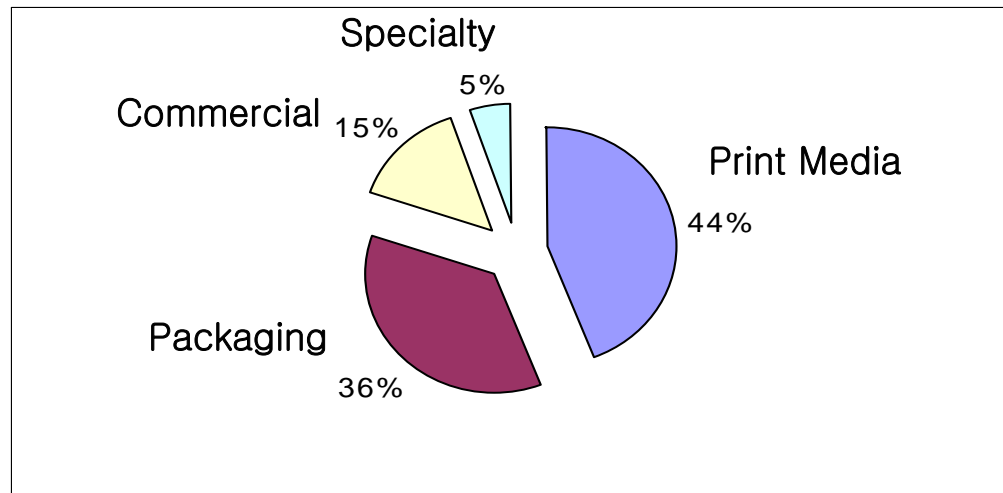


Chart 2. World-Printing Ink Major End-User Markets 1998



Demand Trends

Main end user markets of printing ink

1. Print media
 - newspaper
 - magazine & books
2. Packaging
 - paper & board packaging
 - plastic packaging
 - metal & glass packaging
3. Commercial
 - commercial printing
 - stationery
 - direct mail & advertising
4. Specialty
 - security
 - textile printing

Table 3. North America–Consumption of Raw Materials in Printing Ink 1997

Type	Quantity (Millions lbs)	Value (Millions US\$)
Hydrocarbon Solvents	925	110
Oxygenated Solvents	180	80
Resins	532	525
Pigments	438	770
Additives	180	80
Total	2,150	1,540

Source: Impact Marketing Consultants

Table 4. North America–Ink Resin Consumption 1997

Resin Type	Consumption(%)
Rosin	36
Hydrocarbon	18
Alkyds	13
Acrylic	10
Others	23

Source: Impact Marketing Consultants

Table 5. Typical Resin Found in Common Printing Ink Formulation

Ink Type	Resin
Metal Decorating Publication Gravure	Alkyds, Melamine Modified Rosin Hydrocarbon
Flexo, Packaging Gravure	Cellulose, Polyvinyl Acetate Polyamide Resns
Water-based Flexo, Gravure	Acrylic, Maleic

Source: Fachhochschule Stuttgart

Why water-based ink formulations ?

- Reduced potential for discharging toxic substances
- Reduction of VOCs emitted to the atmosphere into the water system
- Reduces the potential for fire and explosion, thereby eliminating some of the costly provisions and regulations required for the flammable solvents and inks
- Reduces the amount of hazardous wastes
- Improves the working conditions in the plant
- Brings the firms into compliance with almost every regulations

Water-based Inks

Several advantages :

- Non-toxic and non-flammable
- Increased life of stereo and photopolymer plates
- Sharper printings
- Low residual print odor, or none at all
- Less maintenance costs

Disadvantages :

- Less pigment choice
- Inferior ink gloss
- Slow drying, with consequentially higher energy costs and slower production runs
- Problems with multicolor printing due to substrate distortion from water absorption

Chart 3. Typical Solvent-Based Flexo Ink Formulation

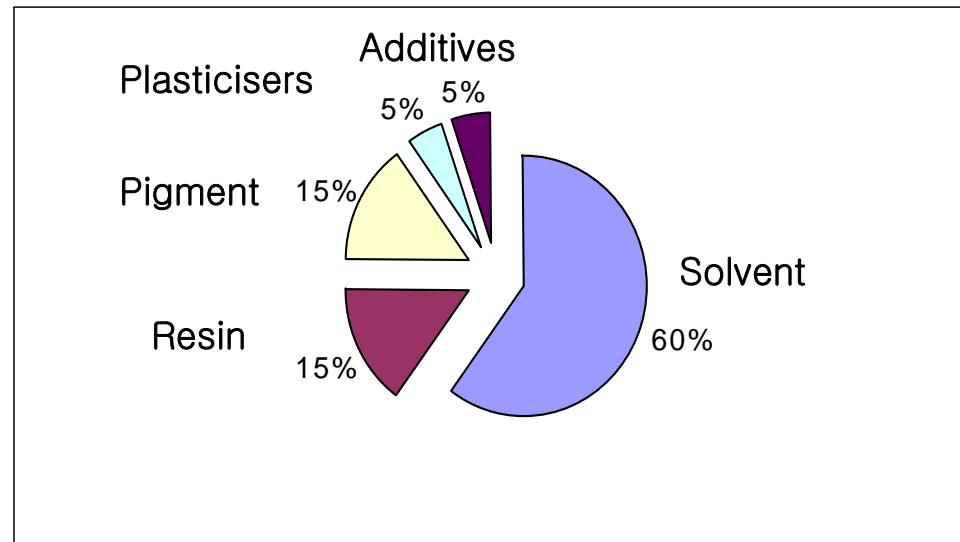
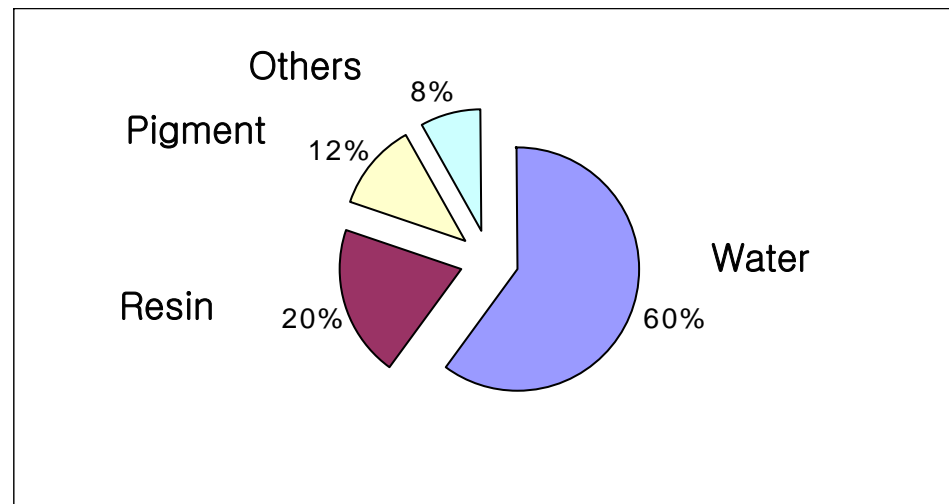


Chart 4. Typical Water-Based Flexo Ink Formulation



(1)

• SAA Varnish , pigment Ink base
RFE let down

Varnish Formulation

Ingredient	Amount (wt%)
SAA Resin	30
H ₂ O	45
Ethylene glycol	20
NH ₄ OH (19%)	5
Total	100

(II)

Ink base Formulation

Ingredient	Part
Glass bead(1.5~2mm)	60
Water	13
Varnish	15
(silicon)	0.5
Wetting agent	1
Wax(PE)	5
	15

(III)

Ink let down formulation

Ingredient	Part
base	50
RFE	35
(mineral oil)	0.2
(silicon)	0.5
Water	15

Graphic Arts Market in Korea

1. water -based (w/b) flexo ink market

existing market

- very popular in paper
- corrugated board and shopping bag: low quality
- grinding vehicle : using ASR
- letdown vehicle: using both RC emulsion and conventional emulsion
- market volume:
 - grinding vehicle: about 1,000 ton/yr
 - letdown vehicle: about 2,000 ton/tr

emerging market

- milk carton & pre -print corrugated board(PPCB) : high quality
- need high performance resin (emulsion)
- two companies have introduced printing technology from ink maker and are producing PPCB which is using w/b ink of licensor.
- market volume: . very small but has good prospects
 - .depending on application not regulations

Graphic Arts Market in Korea

2. w/b gravure ink market

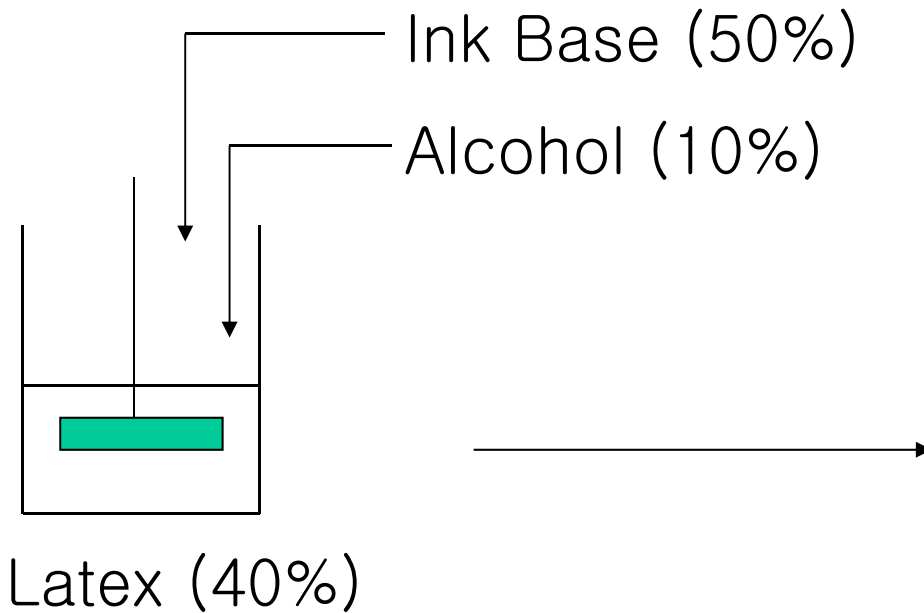
- not familiar with w/b , mainly solvent -based market
- new field market in w/b
- possible niche market : plastic film(treated polyolefin, PET) & PVC wallpaper
- need high performance resin(emulsion) such as acryl/urethane or acryl/ester
- market volume:
 - very small but good prospects
 - depending on application not regulations
 - possibility of substituting solvent - based gravure ink

잉크용 에멀전 수지 : 분석 방법 - 1차 물성

- 분자량 : GPC
- 점도 : Brookfield Viscometer
- 입자 크기 : Particle Size Analyzer (BIC & CHDF)
- 산가 : KOH 적정법
- 고형분 함량 : 중량법

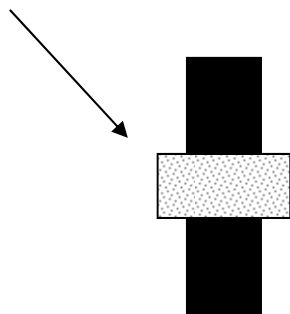
잉크용 에멀전 수지 : 분석 방법 - 2차 물성

• 잉크 제조 과정



• 테스트 과정

시간에 따른
혼합액의
1. 층분리도
2. 점도변화



종이위에 코팅한 후
3. 은폐력
4. 내마모성
5. 전이력

수성 잉크용 수지

- : , , PVP, PEO, PAAm
 ,
 가
- (colloidal dispersion) : alkali soluble resin
- () :

수성 잉크용 수지

		~	()
	~ 0.001 μm	0.001 ~ 0.1 μm	0.1 μm ~
	()	(/pH)	()
	~ 2	~ 10	10 ~
	A	B ~ A	C
	A	B	C
		가	가
	A	B	C ~ B
	B	B ~ A	A
	B	B ~ A	A
		&	

A: good, B: moderate, C: poor

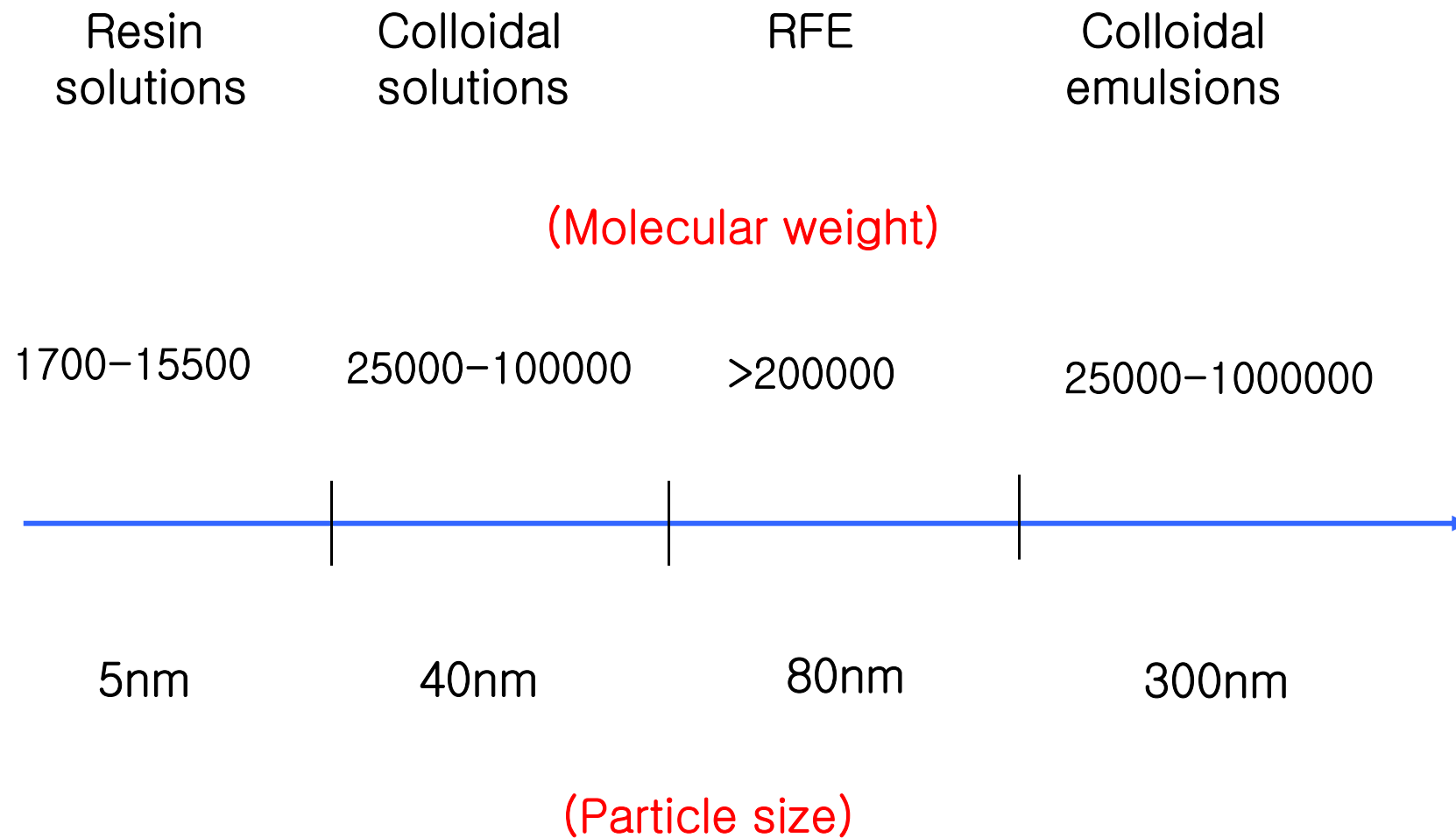


Fig.1 Molecular weight and particle size of acrylic polymers

Ink and OPV performance

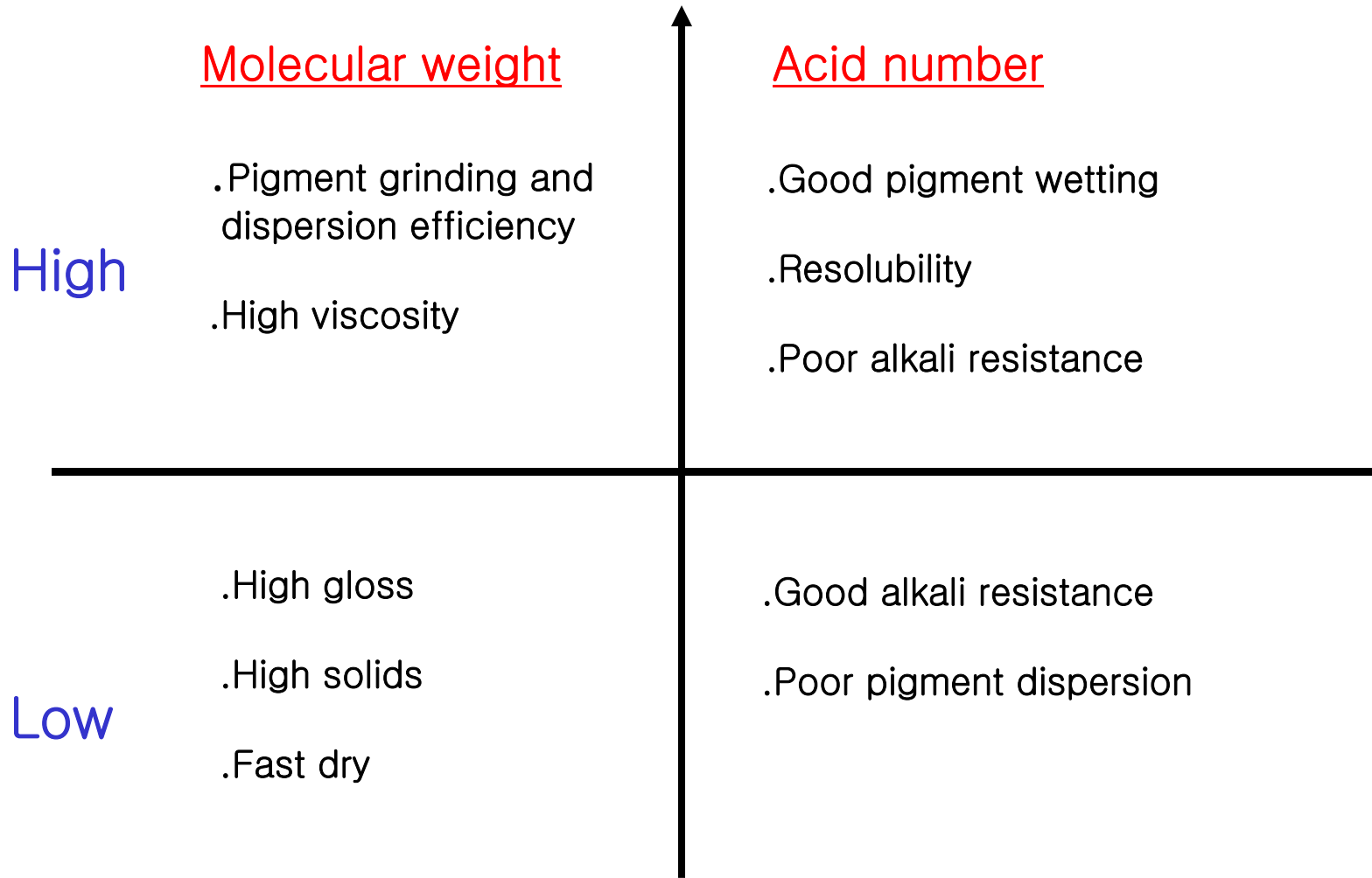
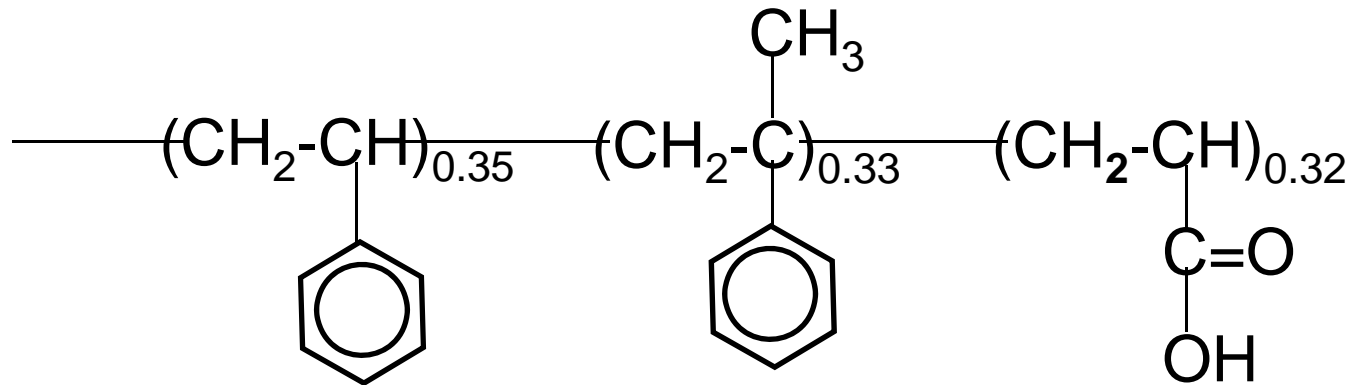


Fig.2 Comparison of ink and OPV performance

SAA (I)



◆ **Styrene / α -methyl styrene / acrylic acid**

◆ **Random**

◆ **Alkali** **water-soluble**

◆ **Mw & Tg** **grade**

수분산 수지

- , , ,
,
- () : conventional emulsion
- () : soap-free emulsion
- support resin : resin-fortified emulsion
(S.C.Johnson社 RC emulsion)

RFE 수지 (I)

-conventional emulsion

emulsion

- (ASR)

- , ()

&

- newtonian

- (, ,)

-

-

RFE (II)

- ◆ Support resin / 가
- Emulsion .
- Emulsion .
- ◆ Support resin / Morphology
- . (Core/shell)
- ◆ Support resin ?
- ♣ Water-soluble resin (PEO, PVP)
- ♣ Water-dispersible resin (Aliphatic PU, Silicon ethylene oxide copolymer)
- ♣ Alkali-soluble resin (SAA, SMA, EAA, EMAA)
- ♣ RFE 2,000~6,000g/mol .
- ◆ / emulsion polymer?
- ♣ Emulsion polymer 가 .
- ♣ $M_n = 10^5 \sim 10^6$ g/mol
- ♣ Tg, , 가
- ♣ , ,
- ◆ Support resin functionality thermosetting resin .

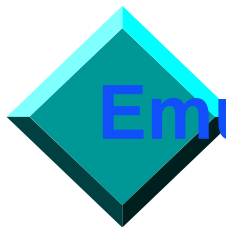
Resin Fortified Emulsions

Physical Characteristics :

- Ultra Fine Particle Size
- Near Newtonian Rheology (Solution - Like)
- Excellent Shear Stability
- No Anionic Surfactant Content
- Carboxyl & Hydroxy Functionality
- Blend Compatibility

Resin Fortified Emulsions

	Solutions (Alkyds)	HCC RF Emulsions	Conventional Emulsions
Appearance	Clear	Translucent	Opaque
Particle Size	Solution	40~80 nm	100~3000 nm
Molecular Weight	$10^3 - 10^4$	$10^5 - 10^6$	$10^5 - 10^6$
Rheology	Solution	Near Solution	Pseudoplastic
Gloss	Very High	High	Low to Semi
Pigment Dispersion	Excellent	Excellent	Poor
Shock Resistance	Excellent	Very Good	Poor to Good



Emulsion for Waterborne Ink & Paint

Products	Features
SAA Resin	<ul style="list-style-type: none">• ST, α-MST and AA terpolymer
RFE	<ul style="list-style-type: none">• Emulsion using SAA resin as a surfactant• Let-down Vehicle• Excellent in Rheological Property
Conventional Emulsion for good opacity	<ul style="list-style-type: none">• Conventional Emulsion• Acid group existed on the surface and inside of Latex particles• Let-down vehicle• Good in Hiding Property
Core-shell type Emulsion	<ul style="list-style-type: none">• Core-shell type Latex• Acid group existed on the surface of Latex particles• Let-down vehicle• Good in Adhesive Property on the surface of Plastic and metal

¹ ST = Styrene, AA = Acrylic Acid, α -MST : α -methyl styrene

RFE Resins for Let-Down Vehicle

	Joncryl-74	Joncryl-77	Joncryl-87	Joncryl-89
Appearance	Translucent	Translucent	Translucent	Translucent
Non-Volatiles (%)	48.5	46.0	48.5	48.0
MW	> 200,000	> 200,000	> 200,000	> 200,000
Acid Number	50	55	50	56
Density (g/cc)	1.05	1.04	1.04	1.04
pH	8.3	8.3	8.3	8.3
Viscosity (cps)	600	500	1,000	500
Tg ()	-16	21	100	98
MFFT ()	< 5	20	> 80	> 80

RFE

Properties	R F E	
	Joncryl-89	L-370
Mn	9,900	18,000
Mw	480,000	315,000
PDI	48.4	17.6
Particle Size	80	70
Tg ()	98	-
(%)	48	48.5
MFFT ()	83	85
pH	8.3	8.0~8.5
Viscosity (cps)	500	800~1200
Acid Number	56	70
Monomer	St/Acryl	St/Acryl

RFE 중합 Procedure

SAA resin solution & pH

(Feeding : 2)

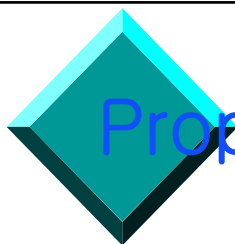
post reaction (45)

Polymerization recipe of RFE resins for water-based flexo ink

(unit : g)

Properties	HCC-89-A	HCC-89-B
ST	218.8	218.8
SAA resin ¹	72.9	72.9
Initiator & Additives	8.1	9.4
DI water	265.0	265.0

(SAA resin¹ : soluryl-70)



Properties of Tested Samples

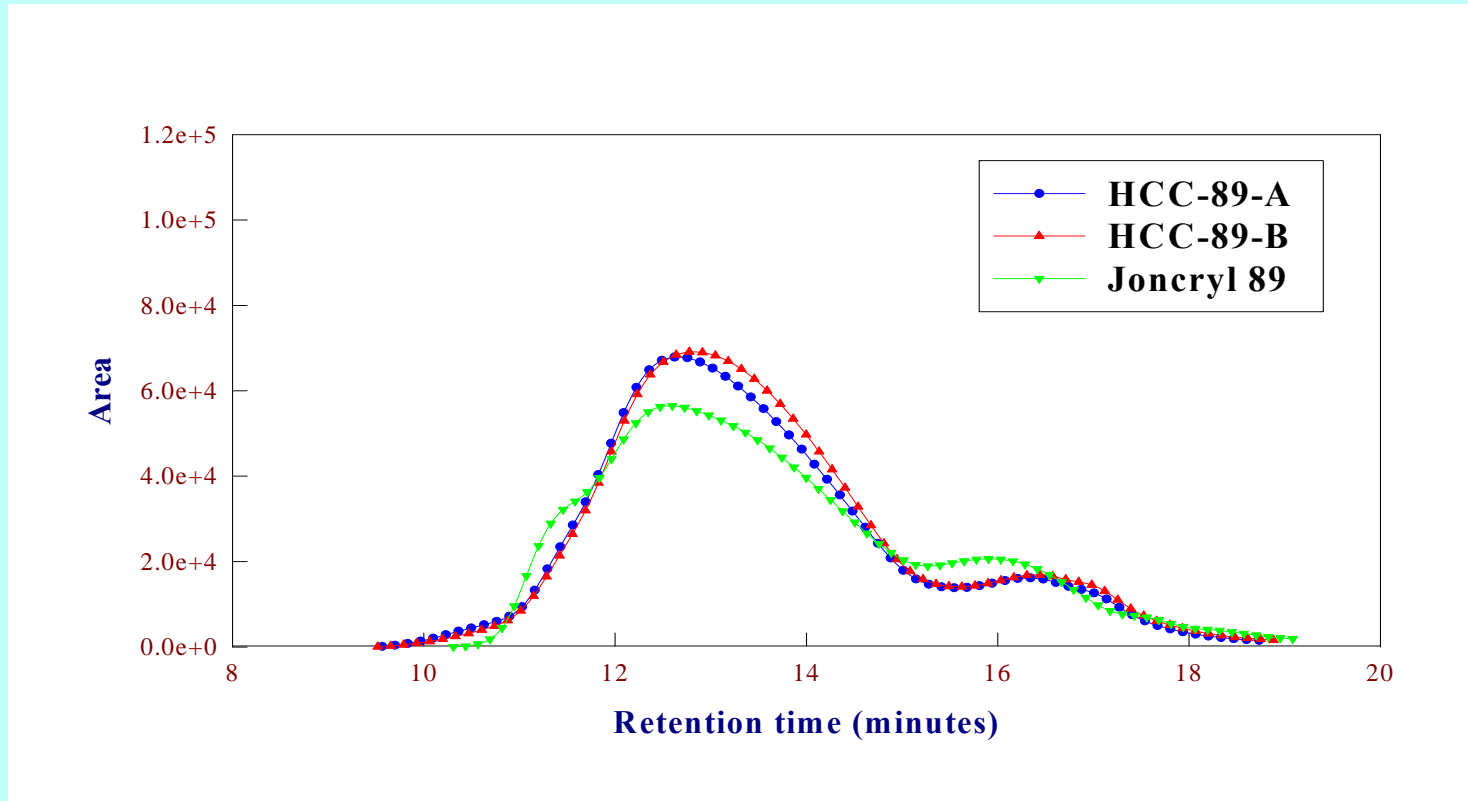
☞ Comparison of properties between Joncryl-89 and HCC's Samples

Properties	Competitor	HCC-89 -A	HCC-89 -B
Particle Size (nm)	80	81	85
Tg (°C)	98	98	98
Solid Content (%)	48.0	50.7	50.4
MFFT (°C)	83	83	83
Acid Number	56.0	58.7	59.2



Properties of Tested Samples

- Comparison of molecular weights & molecular weight distributions between Joncryl-89 and HCC's Samples



Test Result of RFE from Flexo Ink customer

Properties	J-89	HCC-89-A
Color	-	Same
Hiding	-	Same
Transferability	-	Same
Viscosity (Sec)	14.5	14.0
Water Resistance	-	Same
Anti-friction	-	Same
DOI ¹	-	Same
Gloss (60°)	21	22
Dispersing Ability	-	Same

¹ Distinctiveness-of-image

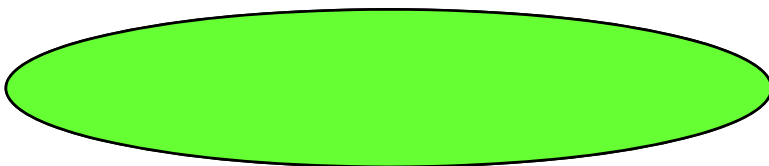
Lab & Pilot

	Lab. sample	2	3
(nm)	Dn : 74, Dw : 81	Dn : 77, Dw : 82	Dn : 75, Dw : 81
(g/mol)	Dn : 19211 Dw : 491589	Dn : 19334 Dw : 499153	Dn : 19824 Dw : 501260
(cps)	800	780	800

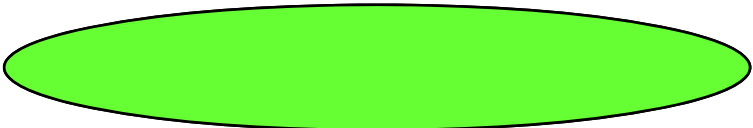
Soluryl R-90

Field Test

	Joncryl-89	2	3
(sec)	14.5	13.9	14.0
1 (sec)	32.0	14.8	17.0
	Standard		
	Standard		
	Standard		
	25	28	20
Gloss	21	22	22
Density	2.43	2.45	2.50



Properties		
	L-361	D-485
Mn	29,800	8,700
Mw	256,000	60,200
PDI	8.61	6.92
Particle Size	125	200
Tg ()	90	90
(%)	50	50
MFFT ()	80	78
pH	7.8	7.7
Viscosity (cps)	1500	2000
Acid Number	30	80
Monomer	St/Acryl	St/Acryl



- - Hydrophilic shell
 - Hydrophilic shell (가)
 - Acrylic acid & Methacrylic acid

- - Acid number
 - Hydrophobic core
 - Particle size & particle size distribution

- Morphology
 - Core/Shell & Simple Particle

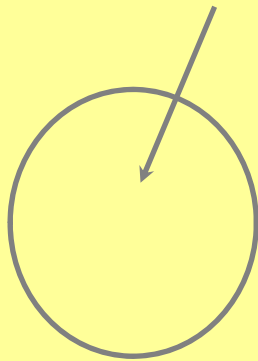
Emulsion

Model

D-485

Grade

Poly(ST-AA-MAA)



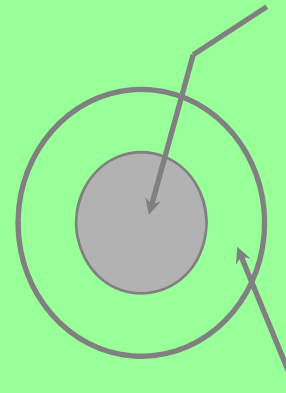
※ Initial pH = ~4

(pH 5 AA
MAA
)

Lucidene-361

Grade

Poly(ST-MMA)



Poly(EA-AA-MAA)

※ Inverse core-shell
emulsion polymerization

Conventional Emulsion의 기본 Recipe

Chemicals		Recipe
Monomers	Styrene	87.8
	Acrylic Acid	8.3
	Methacrylic Acid	3.9
DIW		100.0
		0.4
		1.0
Buffer		0.4
Neutralizing Agent		1 ~ 1.5
Total		202.8~ 203.3

- : 80°C ~90°C

- : 5 Hrs

에멀전 중합 Procedure

Pre-emulsion (Monomer + DIW +)

(DIW + + Buffer + Pre-emulsion)

Pre-emulsion (Feeding : 2 ~ 3)

Neutralization



Properties of Tested Samples

Comparison of properties between Daiwon-485 and HCC's Samples

Properties	Competitor	Conventional A	Conventional B
Particle Size (nm)	200	200	190
Tg (°C)	90	95	95
Solid Content (%)	50	49	49
MFFT (°C)	78	80	80
pH	7.7	7 ~ 8	7 ~ 8
Viscosity (cps) ¹	2,000	2,170	1500
Acid Number	80	82	75
Component ²	ST, AA	ST, AA	ST, AA

¹ Brookfield Viscometer, LVT Spindle No. 63, RPM 30, Temp = 15 °C

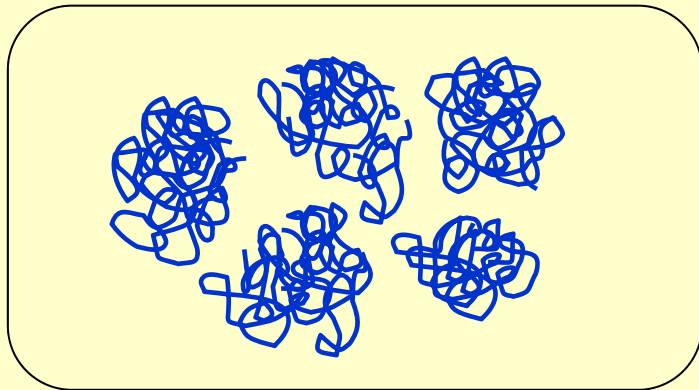
² ST = Styrene, AA = Acrylic Acid

Experimental Design (E-80)

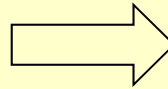
• *First Polymerization (hydrophilic polymer)*

Monomer : EA & MAA &

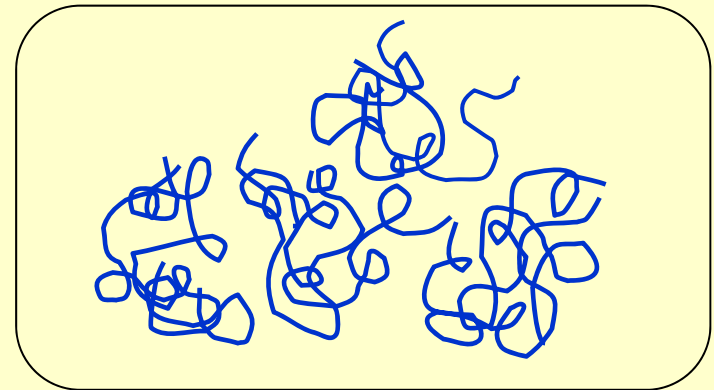
pH : 3.0



Ammonium
Hydroxide



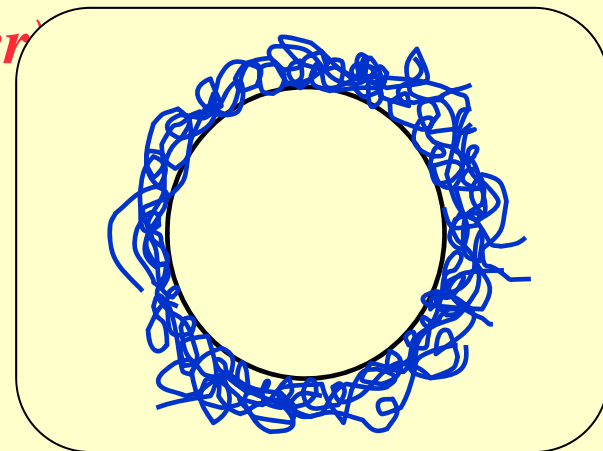
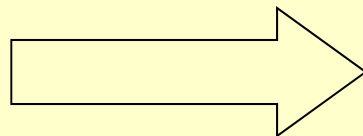
pH : 8.0



• *Second Polymerization (hydrophobic polymer)*

Monomer : Styrene & Acrylate

pH : 8.0



잉크용 에멀전 수지 (E-80) : 기본 Recipe

Initial Charge	Water	950.0
		12.0
	Sodium bicarbonate	3.0
Initial Initiator	Water	180.0
		3.5
1st Stage Monomer Mixture	Methacrylic acid	53.7
	Ethyl acrylate	214.7
	CTA	5.2
		variables
2nd Stage Monomer Mixture	Styrene/Acrylate	1073.6
	CTA	16.1
		30.0
2nd Initiator	Water	180.0
		7.5
Chaser	Water	20.0
		2.2
TOTAL		2829.3

Soluryl E-80: Lab 실험 결과

<입자크기 조절법>

1) 1st stage polymer의 분자량

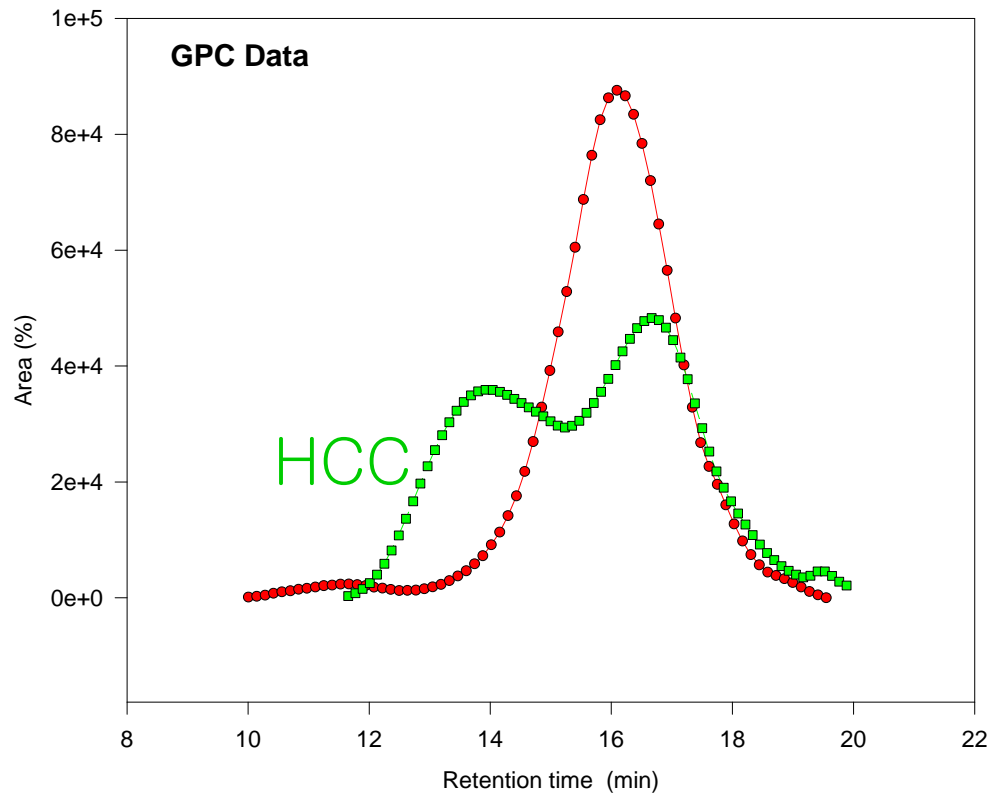
Mn(g/mol)	Dn(nm)	Dw(nm)
27521	73	79
30510	83	93
43365	115	132
61102	188	211

2) 친수성 모노머의 함량

Monomer 함량	Dn(nm)	Dw(nm)
10	179	210
5	155	182
3	115	132
0	93	114

잉크용 core/shell1 에멀전 수지 (E-80)

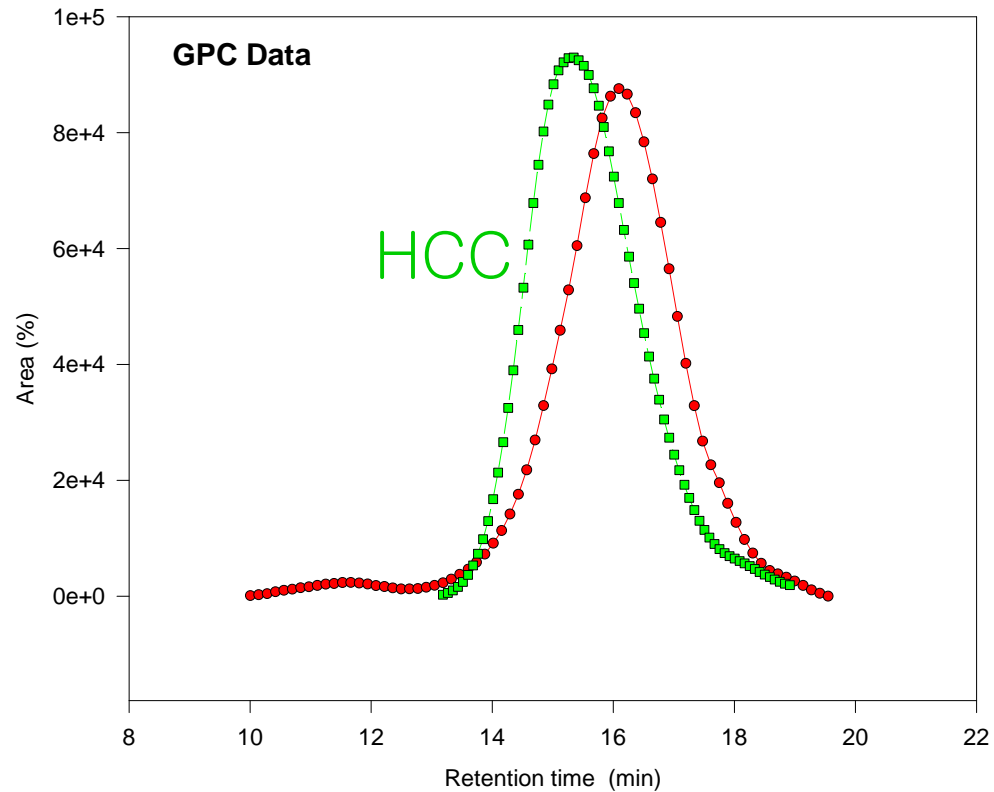
- 분자량 (2단계 CTA 효과 : 친수성)



분자량 분포 : 1단계 (CTA 2%) & 2단계 (CTA 2%) 중합체 - 2 peak

잉크용 core/shell1 에멀전 수지 (E-80)

- 분자량 (2 단계 CTA 효과 - 소수성)



분자량 분포 : 1단계 (CTA 2%) & 2단계 (CTA 1%) 중합체 - 1 peak

Soluryl E-80: Lab 실험 결과

<잉크안정성>

1) acid number

Acid number	상분리 층의 높이(cm)
0	7.7
35	1.6
70	4.0
100	9.0

2) 입자크기

입자크기(Dn) (nm)	상분리 층의 높이(cm)
188	6.3
115	1.3
83	1.1
73	1.1

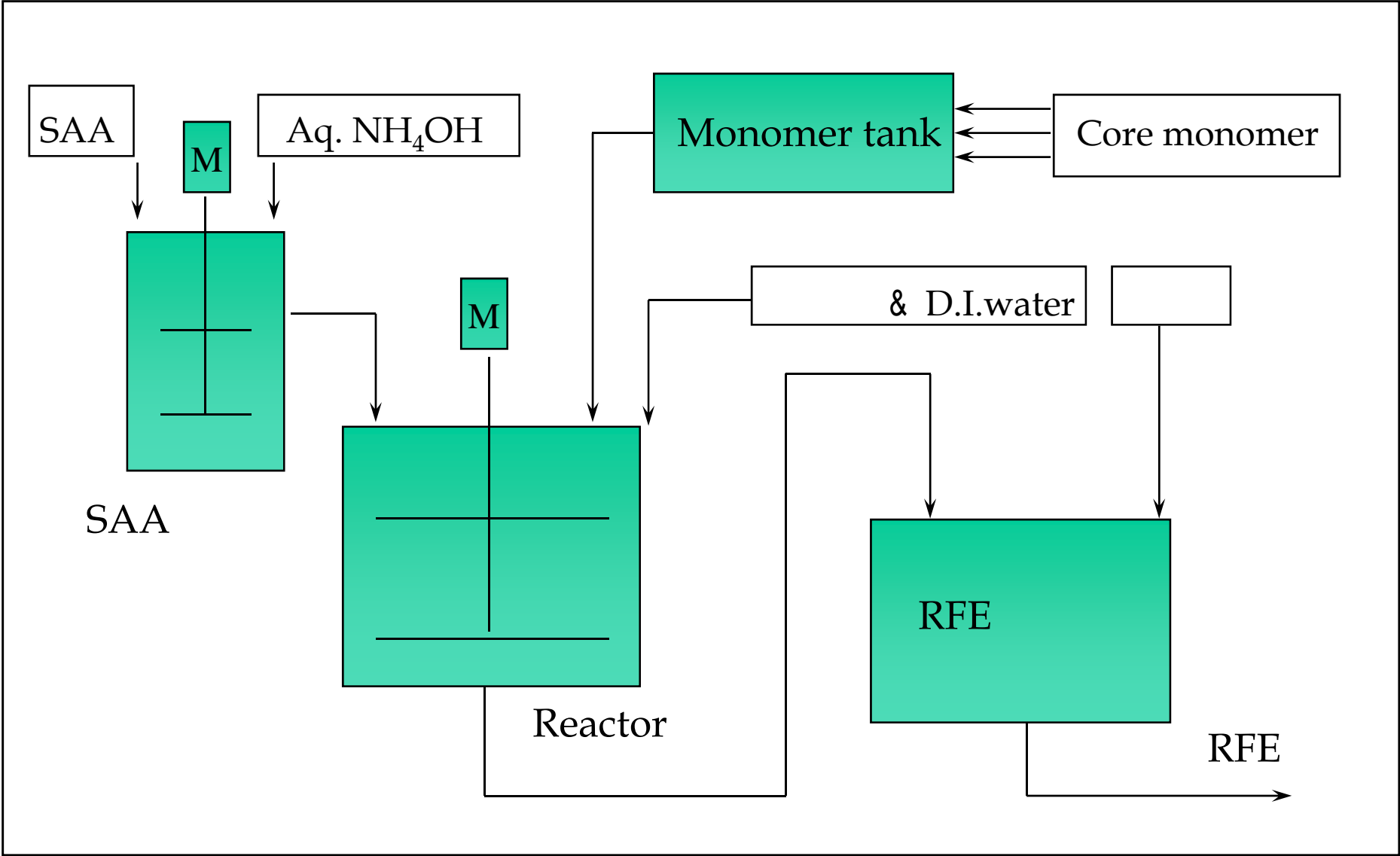
SOLURYL E-80 가 ()

물 성	1차 시생산품	2차 시생산품	3차 시생산품
입자 크기 (nm)	Dn : 117, Dw : 135	Dn : 118, Dw : 135	Dn : 115, Dw : 131
분자량 (g/mol)	Mn : 43965 Mw : 377552	Mn : 42588 Mw : 416003	Mn : 45413 Mw : 358405
산 가	31	31	31
점 도 (cps)	1200	1600	1500
pH	8.0	7.8	7.9

Soluryl E-80 시제품 평가 결과(II)

물 성	Lucidene-361	Soluryl E-80
점 도(sec)	15.5	15.3
전 이 력	standard	동일
침 전	standard	동일
층 분 리 (mm/10cm)	13	13
내 마 모 성	standard	동일
은 폐 력	standard	동일

RFE PROCESS



환경 친화 제품
(수용성 수지)

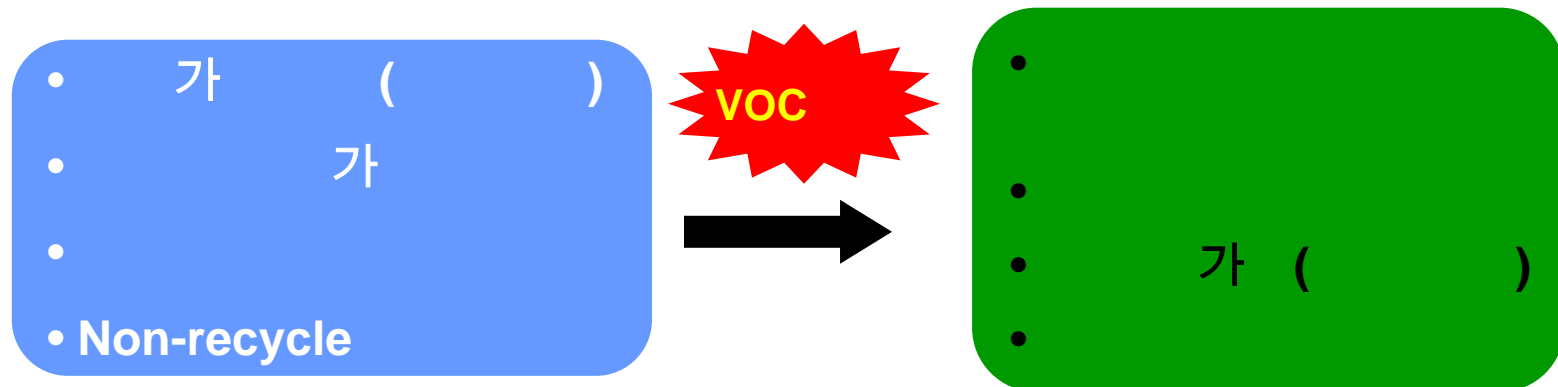
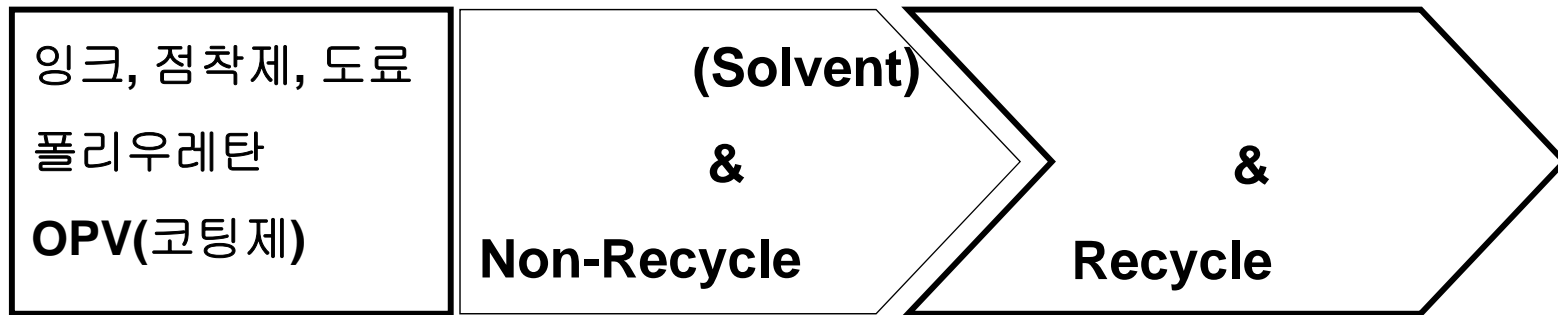
Hanwha Soluryl Resin



1.

■ 인체에 무해한 환경 친화적 제품 요구

분야



2. HCC

SAA(수용성 수지)

- '96~'98 : 공기반 과제 수행(연세대, 동양잉크(주) 공동)
- '98~'99 : Pilot Plant 설치, 시운전 실시
- '99. 9.~ : 상업 판매 실시 (Brand Name : Soluryl-70)

RFE(수지보강 에멀전)

- '97~'99 : 공기반 과제 수행
- '99. 3. : 3 Grade 제품 개발 완료
- '99. 9.~ : 상업 판매 실시 (Brand Name : Soluryl E-80, R20, R90)
(동남아, 호주 및 미국 지역으로 200톤 판매, 금년 1,000톤 수출 예상)
- '00. 5 : 도료용 Emulsion 개발 완료. 상업화 준비중

점착제(PSA), 코팅제(OPV)

- '00. 5. : 수성 점착제 개발 완료. 상업 판매 준비중

기술인증 및 특허

- SAA : - 국내 신기술 인증 획득 (KT : Korean Technology , 과학기술부, 1999)
- 제조 특허 3건 등록 (국내) 및 PCT 출원중(해외)
- RFE : - 국내 및 해외 특허 출원중 (2건), KT 획득(과학기술부, 2000)

3. HCC

▶ 용도

- 수성 잉크, 도료 및 점착제의 유기용제를 사용하지 않는 **RESIN** 및 **EMULSION**
- 수성 후렉소 잉크, 고광택 하이드로 코팅제, 수성 점착제, 지대/포장재 내부 코팅제, 플라스틱/목공/금속 표면 코팅제

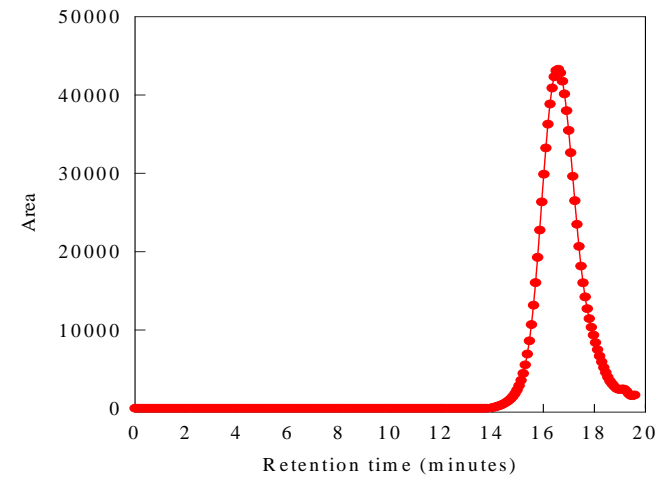
▶ 제품 종류

- 잉크 분야 : **SOLURYL- 70, SOLURYL R-90, R-20, E-80**
- 도료 분야 : **SOLURYL R-40**외 **HASP**
- 코팅(OPV) 분야 : **SOLURYL HG 80**
- 점착제(PSA) 분야 : **SOLURYL P100**

▶ SOLURYL 제품의 특징

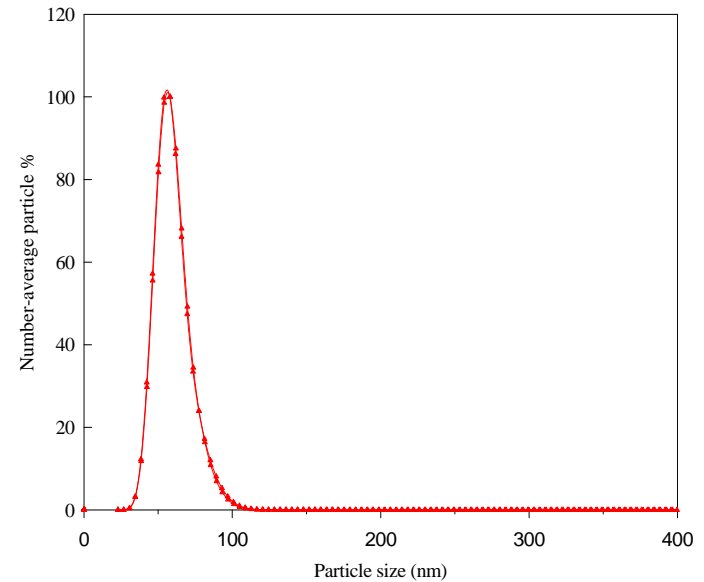
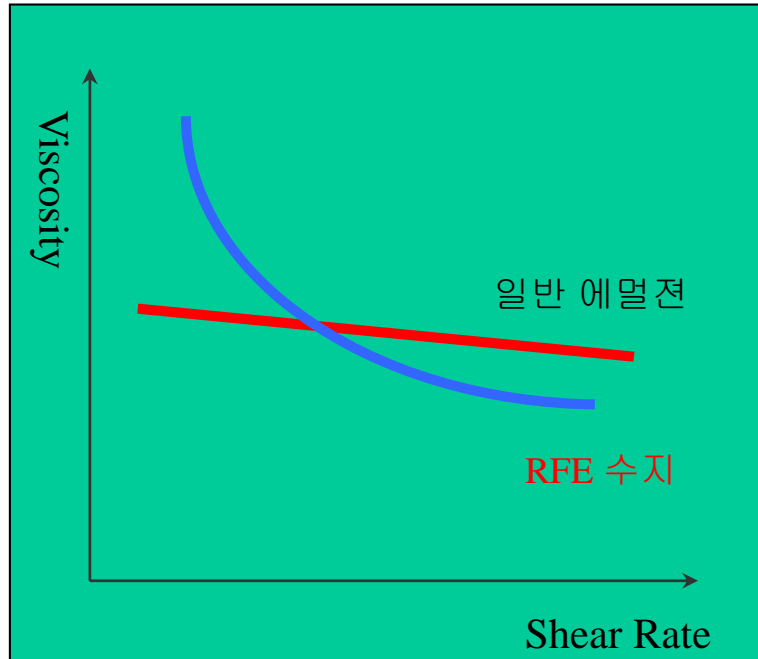
- 환경 친화적 : 용매로 물을 사용하므로 **VOC**배출이 없고, 코팅제의 경우 코팅이 물에 녹으므로 종이의 재활용(**Repulping**)이 가능함.
- 작업성 우수 : 휘발분 함량이 낮아 거품발생이 적음.
- 인쇄성, 전이성, 광택이 우수함.

SAA



- Continuous Bulk Polymerization Process
 - : 연속반응기 및 휘발분 제거장치를 설계하여 제품 생산에 적용 하였으며 균일한 반응조건으로 제품의 균일성이 뛰어남
- Uniform Molecular Weight
 - : 분자량이 작으면서도 분자량분포가 좁음

RFE



- Newtonian-like Flow
: Shear rate에 따라 점도 변화가 크지 않음
- Uniform Particle Size
: 입자 크기가 작고 입도분포가 좁음

Trends for the future

- Polymers for pre-printed corrugated, which require no zinc or zirconium to reach 232 °C hot mar resistance
- Dispersion resins, which develop chip quality gloss and transparency in conventional media milling equipment
- Corrugated vehicles, which require half the resin solids of conventional systems allowing for very low cost inks
- Film printing polymers, which wet out olefins without the addition of any VOC contributing alcohols
- News flexo polymers, which virtually eliminate second impression set off
- Polymers systems for waterborne publication gravure

Major New Developments

To enhance the potential of w/b ink attempts :

- .Decreasing the amount of inks printed per square meter of substrate
- .Increasing the solids in the ink
- .Designing the binder in such a way that it releases the water faster from the ink film
- .Modifying the design of the printing press

- .Improvements in ink formulations
- .Research in pigment development to increase color choice
- .Research in the field of hybrid and cross-linking resins that are initially water-soluble but change to insoluble after printing